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COMPLEXING BEHAVIOURS OF
I. PYRROLE - 1, 2 - DITHIODICARBOXIMIDE . . . "
II. ETHYL N - PHENYLDITHIOCARBAMATE &
III. N - SULPHINYLANILINE
WITH SOME TRANSITION METAL IONS
AND
COMPLEXES OF RHODIUM (I) WITH SULPHUR MONOXIDE (SO)

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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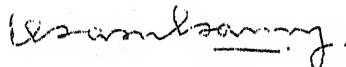
DEPARTMENT OF CHEMISTRY
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DECEMBER, 1982

To
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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



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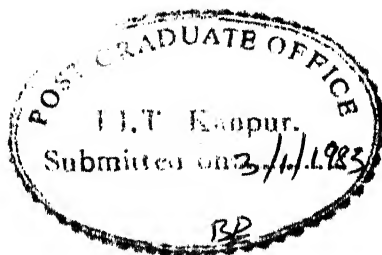
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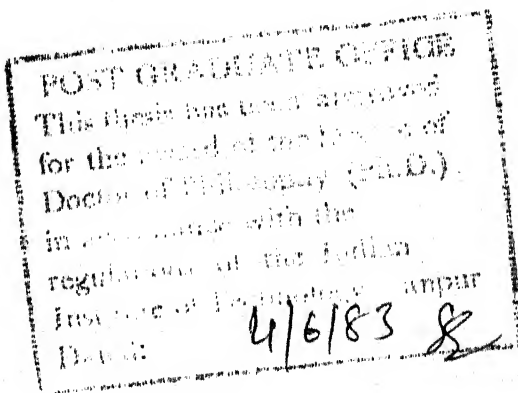
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CERTIFICATE

Certified that the work embodied in this thesis entitled: COMPLEXING BEHAVIOURS OF (i) PYRROLE-1,2-DITHIODICARBOXIMIDE, (ii) ETHYL N-PHENYLDITHIOCARBAMATE & (iii) N-SULPHINYLANILINE WITH SOME TRANSITION METAL IONS AND COMPLEXES OF RHODIUM(I) WITH SULPHUR MONOXIDE (SO) has been carried out by Mr. K.S. ARULSAMY under my supervision and the same has not been submitted elsewhere for a degree.

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PREFACE

The productive pursuit of inorganic chemical research in the field of donor behaviour of sulphur towards metal ions imposes upon the chemist a formidable task; he must know the nature of the bond formed by the metal ions with sulphur-donor. The task becomes even more formidable when the scientific literature shows a definite involvement of the metal-sulphur interaction in biological- and nonbiological-catalytic processes. This has resulted in the exponential growth of research papers related to the syntheses and the design of new model ligands which could form metal complexes mimicing the properties found in the biological system. It is only during such a study that the reflection of the multifaceted aspects of the metal-sulphur bond have been realized and one of the important facets encountered is that the ligands containing sulphur atom or thioamide group not only play a significant role in catalytic (both biological and nonbiological) processes but have antiviral and antitumor activities as well. This interesting aspect of the thioamide moiety has led us to make a little attempt in the direction of the metal interaction with the thioamide group so that a correlation could be sought between the various physico-chemical properties of the transition metal ion complexes with ligands having thiocarbonyl group as one of the potential donors.

The thesis begins with a chapter on a brief literature survey related to the present understanding of the nature of metal-sulphur bond along with the work carried out with the ligands analogous to the ones chosen for the present study. The various reasons which led us to take up the present problem have also been described therein.

The Chapter II encompasses the synthetic details of the complexes of Pyrrole-1,2-dithiodicarboximide with Fe(II), Ru(II), Co(I), Rh(I), Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I) including interpretative discussion of the analytical, spectral and magnetic data providing the reasonable geometries to these complexes.

Chapter III embodies the complexes of Ethyl N-phenyldithiocarbamate with Fe(II), Ru(II), Co(II), Rh(I), Rh(III), Ni(II), Pd(0), Pt(0), Pt(II), Ag(I), Zn(II), Cd(II) and Hg(II). The ligand is acting as monodentate and is bonded to metal ions with one of the sulphur atoms. Their geometries have been suggested in accordance with the supports from spectral and magnetic data.

The synthetic and the structural chemistry of the complexes of N-sulphinylaniline with Mn(II), Fe(II), Ru(II), Co(I), Rh(I), Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I) have been developed in Chapter IV. The ligand being a monodentate, the bonding of the metal ions was restricted exclusively to the nitrogen of the terminal unsaturated group.

Following these chapters on the complexes of the three ligands with various metal ions, the stabilization of sulphur monoxide with rhodium(I) complexes have been discussed in the next chapter. The synthetic, reactivity and structural aspects of the complexes, $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$ ($\text{X} = \text{Cl}, \text{Br}$) with bridging halogen atoms have been described therein.

The last chapter summarizes the work presented in the thesis along with the general comments on the reactivity and affinity of sulphur ligands for metal ions. Due credit has been given with care to the work reported by other authors in the literature. The author is fully responsible for all unintentional oversights and errors which could be traced herein.

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CHAPTER I

CHAPTER I

INTRODUCTION

SCOPE AND OBJECTIVE OF THE WORK

In the recent past much interest has been shown in the reactions of sulphur containing ligands and it is one of the many thrust areas in which significant advances have been made. For quite sometime it has been known that a number of biological processes involve metal ions which coordinate with a wide range of ligands having sulphur, nitrogen and/or oxygen atoms as donor sites. These ligands are usually polyfunctional in nature and are capable of sequestering metal ions in an organic sphere. In addition, a few metal ion complexes have been proved to have anti-cancer [1-8], antiviral and antitumor activities [9-16] in the biological systems. To understand these biological

processes, there has been an increasing interest in the design and syntheses of new model ligands which could lead to metal ion complexes of properties similar to ones found in the biological processes. In the course of such a study, it has been observed that the sulphur containing ligands not only play a significant role in them, but have important pharmacological properties as well. This has led to a great interest in the chemistry of the complexes with sulphur containing ligands. Although most of the chemical reactions have been concentrated towards studies relating to the structures and the nature of bonding of these complexes, the rationalization of the role of M-S bond involved in them is still not clear.

The structure of the metal complex is well defined when the coordination number of the central metal, the stereochemistry, the conformation of the molecule or the complex ion, and the nature of the bond between the metal and the ligand are all known. The nature of the bond itself is closely bound up with coordination number and stereochemistry. An understanding of it and its relationship with other properties is fundamental to the interpretation of the structure and reactivity of a metal complex. It will, therefore, be interesting to correlate the study of different metal ion complexes with various types of sulphur containing ligands. More interesting would be the study of those complexes where there would be an extensive delocalization of charges.

The present work is an attempt in this direction so that a correlation between different physicochemical properties of the complexes synthesized from sulphur-containing-ligands may be sought. This may lead to the understanding of (i) the donor properties of sulphur in general, (ii) the nature of metal-sulphur linkage, (iii) the position of the metals and the ligands in the nephelauxetic and spectrochemical series, (iv) the stereochemistry and coordination number of the transition metal ions and (v) the stabilities of square planar complexes with the ligands having delocalized system.

With the above mentioned objectives in mind, the following ligands have been chosen for the present study: (i) pyrrole-1,2-dithiodicarboximide (PDD), (ii) ethyl N-phenyldithiocarbamate (EPD), (iii) N-sulphinylaniline (NSA) and (iv) sulphur monoxide (SO). The metal ions which have been used for complexation with these ligands are: Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Ag(I), Ru(III), Rh(III), Pd(II) & Pt(II). The stoichiometries, oxidation states of the central metal ions have been studied by chemical analyses. These ligands can act as mono, bi or polydentate towards one or more metal ions. The simultaneous participation of all the donor atoms for the bond formation is virtually impossible because of electronic and stereochemical reasons. There should be various ways in which these donor atoms can interact with the metal ions. Therefore, the modes of bonding and the nature of the bonds formed have been

studied by the infrared, electronic spectral and magnetic susceptibilities studies. Their possible geometries have been tentatively proposed (Table I.1).

Whenever a metal ion forms a bond with a donor atom of a ligand, the possibility is that the bond may be either extremely ionic or extremely covalent in nature. But in the metal complexes, the formation of such extremely ionic or covalent type of bonds would be impossible for the following reasons: (i) the metal and the ligand coordinating atoms are of different size, (ii) they have different electronegativities and (iii) they have different polarizabilities. Hence in most of the cases, the metal-ligand bond will have partial covalent and partial ionic character which will vary within limits from bond to bond. Since the factors deciding the nature of M-S bond in a particular complex are still not well understood, it will not be out of place to give a very brief account of the present position of such a bond which has been reviewed in the following paragraphs.

The strength and the stability of a bond between the metal ion and the donor atom would depend upon several factors like size, electronegativity, the nature of the orbitals involved, their overlapping capacity, etc. The number and the nature of the substituents attached to the ligand donor atoms will also influence the stability of the bond between the metal ions and donor atoms. Since the acceptor metal atom also plays an equal role in the bond formation, the nature of metal-sulphur

Table I.1

Formula, Colour, Geometry and Bonding Scheme of the Complexes

Ligand	Complex	Colour	Geometry	Bonding
1	2	3	4	5
$C_6H_4N_2S_2(PDD)$	$[Fe(PDD)Cl_2(PPh_3)_2]$	Greenish-brown	Octahedral	A
	$[Ru(PDD)Cl_2(PPh_3)_2]$	Blue	Octahedral	A
	$[Ru(PDD)Cl_2(AsPh_3)_2]$	Blue	Octahedral	A
	$[Co(PDD)H P(OPh)_3]$	Brown	Square-planar	A
	$[Rh(PDD)Cl(PPh_3)]$	Dark brown	Square-planar	A
	$[Rh(PDD)(CO)Cl(PPh_3)_2]$	Yellowish-brown	Octahedral or square pyramidal	B
	$[Ni(PDD)(P(OPh)_3)_2]$	Brown	Tetrahedral	A
	$[Pd(PDD)(PPh_3)_2]$	Red brown	Tetrahedral	A
	$[Pt(PDD)(PPh_3)_2]$	Yellowish-brown	Tetrahedral	A
	$[Cu(PDD)Cl(PPh_3)]$	White	Tetrahedral	A
	$[Ag(PDD)(PPh_3)]NO_3$	Pale brown	Trigonal or linear	A
$C_9H_{11}NS_2(EPD)$	$[FeCl_2(EPD)_2]$	Red-brown	Tetrahedral	B
	$[RuCl_2(EPD)_3]$	Dark-red	Octahedral with possibly Ru-Cl-Ru bridge	B
	$[CoCl_2(EPD)_2]$	Green	Square-planar	B
	$[RhCl_3(EPD)_3]$	Red-orange	Octahedral	B
	$[RhCl(PPh_3)(EPD)_2]$	Yellowish-brown	Square-planar	B
	$[NiCl_2(EPD)_2]$	Light green	Square-planar	B

..contd.

Table I.1 (contd.)

1	2	3	4	5
$C_9H_{11}NS_2(EPD)$	$[Pd(PPh_3)_2(EPD)_2]$	Yellow	Tetrahedral	B
	$[Pt(PPh_3)_2(EPD)_2]$	Pale yellow	Tetrahedral	B
	$[PtCl_2(EPD)_2]$	Yellow	Square-planar	B
	$[Ag(EPD)_2]NO_3$	Dark red	Linear	B
	$[ZnCl_2(EPD)_2]$	Yellow	Tetrahedral	B
	$[CdI_2(EPD)_2] \cdot 2C_2H_5OH$	Pale yellow	Tetrahedral	B
	$[HgCl_2(EPD)_2]$	White	Tetrahedral	B
$C_6H_5NSO(NSA)$	$[MnCl_2(NSA)_2]$	Pale pink	Tetrahedral	C
	$[FeCl_2(PPh_3)(NSA)]$	Greyish-green	Tetrahedral	C
	$[RuCl_2(PPh_3)_2(NSA)_2]$	Blue	Octahedral	C
	$[RuCl_2(AsPh_3)_2(NSA)_2]$	Brown	Octahedral	C
	$[CoH(P(OPh)_3)_2(NSA)]$	Pale brown	Square-planar	C
	$[RhCl(PPh_3)(NSA)_2]$	Light brown	Square-planar	C
	$[Rh(CO)Cl(PPh_3)(NSA)]$	Yellowish-brown	Square-planar	C
	$[Ni(P(OPh)_3)_2(NSA)_2]$	Brown	Tetrahedral	C
	$[Pd(PPh_3)_2(NSA)_2]$	Red-orange	Tetrahedral	C
	$[Pt(PPh_3)_2(NSA)_2]$	Pale yellow	Tetrahedral	C
	$[CuCl(PPh_3)_2(NSA)]$	Pale yellow	Tetrahedral	C
	$[Ag(PPh_3)(NSA)](NO_3)$	Grey	Linear	C
	$[Rh(SO)Cl(PPh_3)]_2$	Light brown	Square planar	D
	$[Rh(SO)Br(PPh_3)]_2$	Brown	Square planar	D

A, The ligand is acting as bidentate and is bonded to metal ions with both the sulphur atoms.

B, The ligand is acting as monodentate and is bonded to metal ions with one sulphur atom.

C, The ligand is acting as monodentate and is bonded to metal ions with nitrogen atom.

D, Bonding through S of SO and Cl or Br atoms act as the bridges between $[Rh(SO)(PPh_3)]$ moieties.

bond may be studied under two separate headings: (a) the role of sulphur as donor atom in relation to other donor atoms, when attached to same or similar metal ions and (b) the relative affinities of different metal ions for sulphur-containing ligands.

(a) Sulphur as the donor atom

The polarizability of any coordinating ligand atom is an expected factor influencing the nature of the bond, and that of sulphur falls as follows: $F^- < O^{2-} < Br^- < I^- \ll S^{2-} < Se^{2-} < Te^{2-}$ which is the reverse of the electronegativity series. Sulphur atom being more polarizable in comparison with oxygen, chlorine, bromine or fluorine, the metal-sulphur bond would be expected to be more covalent than metal-oxygen, -chlorine, -bromine and -fluorine bonds. This statement will hold, only when the donor atoms act as ligands in the form of the elementary ions. As mostly this is not the case and the donor atoms exist in the combined form, their polarizability should be different because of the attached atoms or groups, which will change the nature of the bond as compared to that of bonding as elementary ions.

In addition to the σ -type of covalent bond, there may be possibilities of π -bond formation either from metal to ligand or from ligand to metal. Accordingly, the presence of low lying p- or d-orbitals to result in the formation of $d_{\pi} - d_{\pi}$ or $d_{\pi} - p_{\pi}$ bonds by the mechanism of transferring the charge back

to the ligand donor atoms, (S, Se, Te, P, As, Sb, etc.) has got some importance. Thus, when the donor atoms have empty orbitals of suitable symmetry and the metal ions have nearly filled with electrons in the d-orbitals, there may be a strong tendency to form a bond of multiple order by back-donations from metal to ligand, ($M \rightarrow L$). This type of back-bonding may not be possible in the case of metal ions having no or a few d-electrons and ligands having O, N and F as donor atoms, as they do not have any low lying vacant orbitals to accept the metal electrons. However, there can be another possibility of π -bond formation, ($L \rightarrow M$) by accepting the ligand electrons into empty metal d-orbitals. This type of situation is less frequently met with, as the metal ions would normally have enough or more electron density than an optimum σ -system. We can expect this type of binding only in complexes having highly charged metal ions like MnF_6^- , TaF_8^- , CrO_4^{2-} , MnO_4^- , etc.

The back-bonding concept can also explain the bonding difference of the 'hard' and 'soft' metal ions with 'hard' and 'soft' ligand atoms. This concept is successful in explaining the difference in the stabilities of the complexes formed from the ligands having F, O and/or N atom on one hand and S, Se, P and/or As atom on the other hand. As the overlap would be more effective along the internuclear axis, π -bonds will be weaker than σ -bonds and generally they do not exist independently. However, the formation of π -bonds will tend to draw the nuclei involved closer together with a consequent increase in the σ -overlap

and hence an overall gain in bond energy and shortening of the metal-ligand σ -bond. Further, the formation of π -bond will also contribute towards a reduction in the mutual repulsions of the non-bonding electrons, leading to strengthen the bond between the metal and ligand. Though there are views against this kind of extensive π -back-bonding in phosphine and arsine type of complexes for which alternative explanations [17-19] have been given, this back-bonding approach is more successful in explaining certain of the observed facts. From a consideration of both electrostatic and covalent σ -bond models, the strength of bonding to a metal ion is in the order: $RO^- > RS^-$ and $R_2O > R_2S$. However, sulphur atom has vacant d-orbitals, which can be used for $d_\pi-d_\pi$ bonding, which may form with the heavier transition metals and with the early transition metals in low oxidation states. Consequently, if π -bonding occurs, it can cause a reversal of the order to $RS^- > RO^-$ and $R_2S > R_2O$.

Another factor influencing the coordinating ability of a ligand is its total dipolemoment, $\mu = P + \alpha E$ (where P = permanent dipolemoment, α = polarizability and E = field strength). Higher the dipolemoment of a ligand, higher will be its coordinating ability. In spite of the higher polarizability of sulphur atom in H_2S and R_2S , the latter has a greater coordinating ability due to its higher permanent dipolemoment. Though the polarizabilities of S and O atoms are in the order $S > O$, the coordinating ability of H_2S is much lower than that of H_2O because of the

fact that $\mu_{\text{H}_2\text{O}} \gg \mu_{\text{H}_2\text{S}}$ [20]. Hence H_2S will have preferential bonding to cations of higher field strength (higher charge) and the reverse will hold for bonding to cations of lower field strength (lower charge). In general, the coordinating ability of oxygen containing ligands follows the order: $\text{H}_2\text{O} > \text{ROH} > \text{R}_2\text{O}$ and the reverse order holds for sulphur containing ligands: $\text{H}_2\text{S} < \text{RSH} < \text{R}_2\text{S}$.

The nature of the M-S bond in complexes of sulphur-nitrogen chelating agents are similar to those of sulphur ligands. However, the nitrogen atom tends to lower the solubility of the chelates in non-aqueous solvents so that complexes of sulphur-nitrogen ligands are, in general, either sparingly soluble or insoluble in non-polar solvents. From the available data, sulphur-nitrogen ligands appear to give rise to a smaller reduction in the interelectronic repulsion energy than that in S-S ligands. This is presumably due to nitrogen having a low position compared to sulphur in the nephelauxetic series. Consequently, sulphur-nitrogen donors would be expected to give rise to higher values of β than sulphur donors alone.

On the surface, it is apparent that polarizability is the most important factor in determining the reactivity of a nucleophile. However, there is no single scale for nucleophilic reactivities. With reference to $\text{trans-Pt(py)}_2\text{Cl}_2$ as the standard, a scale has been devised to give nucleophilic reactivity

constants (n_{Pt}^0) for different ligands. The values for n_{Pt}^0 for sulphur ligands vary considerably from 3.29 for $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}$ to 7.34 for $\text{S}_2\text{O}_3^{2-}$. It is note worthy that the mercaptide ligand, $\text{C}_6\text{H}_5\text{S}^-$ has the high value 7.17. Ligands with low values for n_{Pt}^0 are Cl^- (3.04), NH_3 (3.06), pyridine (3.13) and Br^- (4.18) and those with highest values for n_{Pt}^0 are tertiary arsines and phosphines, (7.54 - 8.85). These ligands are capable of dative π -bonding to platinum(II) in the transition state [21].

(b) Affinities of metal ions for sulphur

The role of a metal ion for the metal-sulphur σ -bond formation will depend on its ionization potential, electron affinity and ionic or covalent radius. The solvation energy also plays an important role, if the metal-sulphur bond is formed by substitution reaction in solution, due to the different ΔG (free energy change) values in the gas phase and in solution. In addition, the presence of non-bonding electrons in the low lying orbitals on the metal ion also affects the strength of the metal-sulphur bond.

Work has been done [22-24] to correlate the stabilities of complexes with the size and the charge of the metal ions. One of the earliest correlations of the stabilities of complexes was the Irving-Williams series [25,26]. For a given ligand, the different stabilities of the complexes with dipositive metal ions follow the order: $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$. This order arises partly because of the decrease

in size across the series and partly because of ligand field effects. Another important observation is that certain ligands form their most stable complexes with metal ions like Al^{3+} , Ti^{4+} , Co^{3+} , etc., while some others, with metal ions like Cu^+ , Ag^+ , Pd^{2+} , Pt^{2+} , etc. Thus according to the preferential bonding of metal ions and ligands, they have been classified as 'a' and 'b' types by Ahrland [27].

Ahrland and coworkers [28] have proposed that the affinity of class 'b' metal ions for a certain donor atoms depends on the availability of electrons in the metal $(n-1)d$ orbitals for π -bonding. Different explanations have been given for 'a' and 'b' types of behaviours towards halides, which could be extended to sulphur [29-33].

Pearson [34-36] has suggested the terms, "hard" and "soft" to describe the members of class 'a' and class 'b'. The experimental observations suggest that hard acids combine preferentially with hard bases and vice versa. The following set of factors have been proposed that may be responsible for this type of general behaviour of interactions: (i) different degrees of ionic and covalent bonding in the σ -bond, (ii) π -bonding ($\text{M} \rightarrow \text{L}$, $\text{L} \rightarrow \text{M}$), (iii) electron correlation phenomenon, (iv) solvent effects and (v) van der Waals forces.

Besides these "hard" and "soft" acids and bases, there exists a borderline category [37]. Thus, metal ions like Fe(II) , Co(II) , Ni(II) , Cu(II) , Zn(II) , etc. act as borderline

acids and ligands like PhNH_2 , $\text{C}_5\text{H}_5\text{N}$, N_3^- and N_2 act as borderline bases. The members of the same group do not have equivalent hardness or softness. For instance, in the same hard acid group, more polarizable Cs ion will be relatively softer than the Li ion. The presence of a polarizable substituents can also affect their behaviour. For example, pyridine is sufficiently softer than ammonia which is considered as a borderline case, but a reverse situation can also operate in the system, in the presence of electron withdrawing substituent(s) which may reduce the softness of the site.

Jørgensen [18], in order to explain class 'a' and class 'b' character of acids and bases pointed out that the electric dipole polarizability is connected partly with a few of the continuum orbitals and partly with the valence orbitals. If the synergic formation of σ -bonding ($\text{L} \rightarrow \text{M}$) and back-bonding ($\text{M} \rightarrow \text{L}$) is connected with the continuum orbitals of $\text{X}(=\text{S})$, it is reasonable to think of metal being polarized by X. The reason why the chemical softness of hydride ion, R_3P , R_2S and iodide might have something to do with empty orbitals not present to the same degree in H_2O or F^- , is not a question of π -back-bonding to the 3d orbitals of R_3P , R_2S or I^- , but a question of continuum starting at lower energy in these ligands compared to the R_3N , R_2O and F^- .

Klopman [38] elaborated his theory of second order perturbation to heteronuclear molecu] [??] reproducing, with the

exception of H^+ , Ahrland, Chatt and Pearson's series of hard and soft central atoms: $Al(III) > La(III) > Be(II) > Mg(II) > Ca(II) > Fe(III) > Sr(II) > Cr(III) > Ba(II) > Ga(III) > Cr(II) > Fe(II) > Li(I) > Cu(II) > H^+ > Tl(I) > Cd(II) > Ag(I) > Tl(III) > Au(I) > Hg(II)$. From his calculation, it has been concluded that soft-soft interaction results essentially in covalent bonding between an empty and a filled orbitals of comparable energy, whereas hard-hard interactions are charge controlled and determined by Madelung potential. In this treatment, he has taken into account of the solvation energy which modifies very drastically the order of the softness in acids and bases. It is quite conceivable that it will be highly solvent dependent. For instance, acids with high oxidation numbers become relatively softer in non-polar solvents; e.g., $Te(IV)$ coordinates with diarsine (soft base) in dioxane more strongly than $Fe(III)$ and $Cr(III)$ [40].

The complexes of low-spin d^8 ions like $Pd(II)$, $Pt(II)$, $Au(III)$ and the d^{10} ions like $Cu(I)$, $Ag(I)$, $Au(I)$, $Hg(II)$ have high stability constants when complexed with sulphur ligands. Being typically 'b' class, they form strong σ -bonds with soft ligands and also $d_{\pi}-d_{\pi}$ bonds by donation of a pair of electrons to the ligand.

Williams and Hale [41] have deplored the quantitative notion of "hard" and "soft" acids and bases. The controlling factor of the classification is the relative importance of ionic and covalent bonding which has been measured by the value of

$1/(IP \times r_e)$, IP is the ionization potential of the acceptor and r_e is the metal-ligand bond distance. The higher the value of this function, the higher is the ionic character of the bond. The percentage ionic character of a bond, therefore, depends upon the charge, the type of reactants and the solvent (ligand) bound to them. London energies and classical polarization may also be important to certain extent, but as with π -bonding no quantitative demonstration of these effects has been done.

A two-parameter system, expressing the heat of formation of acid-base complexes, has been suggested by Drago and Wayland [42-45],

$$-\Delta H = E_A E_B + C_A C_B$$

where H is the enthalpy of formation of a complex; E_A , C_A are parameters characteristic of acid, and E_B , C_B are parameters characteristic of the base. The E parameters are interpreted as the susceptibilities of the species to undergo electrostatic (ionic or dipole-dipole) interaction and C parameters, as susceptibilities to form covalent bonds. The introduction of E and C parameters enables to predict the enthalpies of reactions and to obtain some insight into the nature of the bonding in various systems. Thus, if we compare the C_A and E_A parameters of iodine and phenol, it appears that iodine is twice as good a "covalent bonder" as phenol, but the latter is about five times effective through electrostatic attraction.

Ahrland [46] has pointed out that the hard-hard interactions are generally endothermic, while the soft-soft interactions are exothermic in nature.

It, therefore, appears from the above discussion that the hard-hard interaction probably is mostly ionic while the soft-soft interaction, covalent in nature, which varies from case to case. Further, the role of π -back-bonding in the soft-soft interaction is still undecided.

One way to demonstrate (to some extent) the nature of metal-sulphur bond is to find the positions of the metal ions and the ligands in the nephelauxetic series. The nephelauxetic effect [47-49] to a certain extent is a measure of covalency in a metal-ligand bond. The numerical value of B (Racah parameter) is a measure of the repulsion between the d -electrons and is found to decrease by 5 to 40 per cent on complexation. Usually the ratio of the electronic repulsion parameters for the metal ion in the complex (B) and that for the gaseous ion (B^0) is denoted by $\beta (= \frac{B}{B^0})$. Thus, if the bond between metal and sulphur atoms is highly covalent, the sulphur ligand should have high nephelauxetic effect or low β value. However, not all sulphur-ligands have low β value. In the following series, ligands are arranged in the decreasing order of β : $F^- > H_2O > RCO_2^- > (NH_2)_2CO$, $NH_3(COO)_2^{2-} \approx en > \underline{NCS}^- > OH^- > CN^- > \underline{SCN}^- > Br^- > (EtO)_2PS_2^- > S^{2-} \approx I^- > (EtO)_2PSe^-$. It is to be noted that this series follows roughly the order of decreasing electronegativity, $F > O > N > Cl > Br > S \approx I > Se$.

The position of sulphur-containing-ligands varies with the types of ligand in the following spectrochemical series:

$I^- < Br^- < SCN^- < Cl^- < (EtO)_2PSe_2^- \approx S^{2-} \approx (EtO)_2PS_2^{2-} < F^- < Et_2NCS^- <$
 $urea \approx OH^- < C_2O_4^{2-} \approx O^{2-} \approx H_2O < NCS^- < glycine < Py \approx NH_3 < en \approx SO_3^{2-} \approx$
 $NO_2^- \approx phen \approx bipy < H^- < CH_3 < CN^- < CO$. Probably R_2S may occur
 between H_2O and NCS^- . As $10 Dq$ is the difference between the
 σ -antibonding effect on the higher subshell (E_g in octahedral
 chromophore, MX_6 or T_2 in tetrahedral chromophore, MX_4) and
 π -antibonding effects on the lower subshell (T_{2g} or E , respect-
 ively), one can rationalize that ligands containing one lone pair
 such as H^- , NH_3 , SO_3^{2-} form only σ -bonds and have large values
 of $10 Dq$. On the other hand, ligands with several lone pairs
 can also have π -bonding effects with the partially filled metal
 ion orbitals leading to decrease of the $10 Dq$ value: $Et_2PS_2^- <$
 $Et_2NCS_2^- < Et_2OCS_2^-$.

The present work deals with the ligands having the follow-
 ing sulphur-donor groups: (i) $-C(S)NHC(S)-$, (ii) $-NHC(S)SC_2H_5$,
 (iii) $-N=S=O$ and (iv) $S=O$. All the four ligands and their
 complexing behaviour with different metal ions will be studied
 in separate chapters and the earlier work regarding the ligands
 having similar groups will be briefly reviewed as in the
 following.

A. Complexes of the Ligands Analogous to Pyrrole-1,2-dithio- dicarboximide

(a) β -Diketones and their sulphur analogues

Werner [50] reported for the first time the chelating
 ability of acetylacetone. Since then the complexes of

acetylacetone and many other β -diketones with nearly all the metals and metalloids have been extensively studied [51-54]. Though these reactions are of intrinsic interest, their investigations have been stimulated by the implications in chemical analyses, catalysis or in biological processes which often arise from their study.

Metal acetylacetonates undergo a wide range of chemical reactions like ligand addition [53], exchange of ligand residues from one metal to another [55], electrophilic substitution in the chelate ring [56], etc. Reactions of metal chelates with aromatic bases and phosphines have been extensively studied [57,58]. It was noted that the adducts of the chelating bases like 1,10-phenanthroline, 2,2'-bipyridyl and 2,2',2''-terpyridyl were quite stable even at relatively high temperatures, whereas the adducts of the ligands like pyridine and picoline easily lost the bases on exposure to air or on heating. Complexes of Ni, Pd, Pt, Zn, Cd, Hg and Pb with thio- β -diketones containing fluorosubstituents have been found to have extra stability [59] which was explained on the basis of electron withdrawing mechanism. Metal β -diketonates react with other metal halides to give exchange products [55]. Analogous reactions of thio- β -diketones have also been reported [60]. It has been observed by the study of these reactions that acetylacetone could not replace thioacetylacetone from square planar bis(thioacetylacetonato)-nickel(II) but after addition of pyridine to give the octahedral complex, replacement did occur [58] which suggested larger 'b'

character of Ni(II) in four-coordinated nickel(II) than that of the metal ion in six-coordinated species. The reverse reaction of thioacetylacetone replacing acetylacetone is observed for Mn(III) and Fe(III) [60]. Such exchange reactions have been found to be useful for preparing thio- β -diketonates. Metal acetylacetonates and thio- β -diketonates underwent electrophilic substitution reactions suggesting the aromatic character of the chelate ring [56,61].

Monothio- β -diketonato complexes, FeL_2 and CoL_2 (LH = thio-benzoylacetone and monothioacetylacetone) [62] have been found to show planar \rightleftharpoons tetrahedral structural equilibrium in solution. In metal complexes of the type, $M(RCS=CHCOR')_n$ (when $n=2$, $M = Pd, Pt, Ni, Zn, Cu$; when $n=3$, $M = Fe, Co, Ru, Rh$) [57,61, 63-67] bonding was found to be through sulphur and oxygen, whereas in complexes of $Ag(I)$, $Cu(I)$, $Tl(I)$, $Cd(II)$, $Hg(II)$ and $Pb(II)$, through sulphur only.

X-ray structural investigations [68,69] of $M(C_6H_5CS=CHCOC_6H_5)_2$ ($M = Pd, Pt$) have shown the pronounced shortening of M-S bond as compared to normal M-S single bond, indicating the considerable degree of π -bonding in it. Further, a marked contraction for the iron atom coordination sphere in $Fe(C_6H_5CS=CHCOC_6H_5)_3$, in going from high spin to low spin states [70] has been detected. The structure of $Zn(CH_3CS=CHCOOC_2H_5)_2$ has been shown [71] to have the two chelating rings in non-equivalent geometry. Tetrahedral geometry has been assigned to this compound.

It has been shown that thiothenoyltrifluoroacetone could be used as a colorimetric reagent for lead, zinc and cadmium with which it forms coloured chelates, whereas the β -diketones of these elements are colourless [63]. Though the quantitative aspects of the use of these ligands are not known, the technique has been used for the determination of cobalt [71]. The solubility of the metal chelates in nonpolar solvents coupled with low solubility of the ligands in water allowed the extraction of metal ions from an aqueous to an organic phase. Uhlemann and Mueller [71-74] have shown the extraction of Cu(II), Ni(II) and Co(II) with thio- β -diketones into n-heptane or carbon tetrachloride from solutions of higher acidity than the corresponding β -diketones. However, the oxidation of these ligands limit the use of these reagents for solvent extraction.

The complexing behaviours of dithio- β -diketones are well known in the literature [75-80]. Several chelates of dithioacetylacetones have the general formula, $M(CH_3CS=CHCSCH_3)_n$ (when $n=3$, $M=Cr, Fe, Co, Ru, Rh, Os$ and Ir ; when $n=2$, $M=Co, Ni, Zn, Pd$ and Pt). Mixed chelates of the mono- and dithioacetylacetone ligands of Ni(II) and Co(III) have also been prepared [77,81]. The structure of $Fe(CH_3CS=CHCSCH_3)_3$ has been determined [82-84] by X-ray studies. The crystals are composed of discrete molecules of the neutral complex with six sulphur atoms arranged about each iron atom in a slightly distorted octahedral fashion. It is interesting to note that $Fe(CH_3CO=CHCOCH_3)_3$ is a high spin complex and $Fe(CH_3CS=CHCOCH_3)_3$

exhibits thermal equilibrium between $S = 5/2$ and $S = 1/2$ states, while $\text{Fe}(\text{CH}_3\text{CS}=\text{CHCSCH}_3)_3$ is definitely a low spin complex [85].

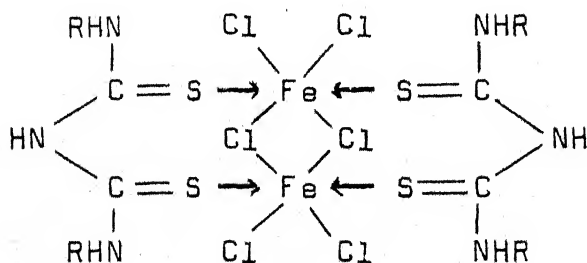
The structural aspects of $\text{Rh}(\text{CH}_3\text{CS}=\text{CHCSCH}_3)_3$ as determined by X-ray method [86] indicated six sulphur atoms around each rhodium ion arranged in a distorted octahedral configuration at distances ranging from 2.314 Å to 2.333 Å. Although the distortion was found to be essentially due to the opening out of intra-ligand S-Rh-S angles from the regular 90° to about 97° , carbon to sulphur and carbon to carbon internuclear distances in the ring remained unaltered showing extensive delocalization of the electrons in the ring.

The structural studies [76,87] of $\text{M}(\text{CH}_3\text{CS}=\text{CHCSCH}_3)_2$ (where $\text{M} = \text{Co(II)}, \text{Ni(II)}$) revealed a square planar environment of four sulphur atoms around the metal ion and an S-M-S intra-ligand bond angle of 97° . Although the molecule as a whole was not planar, it was somewhat folded with the dihedral angle of 60° between the MS_4 and ligand planes. The average metal-sulphur bond distance was reported to be 2.17 Å. The structural details [88] of $\text{Zn}(\text{CH}_3\text{CS}=\text{CHCSOC}_2\text{H}_5)_2$ showed that the molecule consisted of monomeric unit of the complex with each unit having a tetrahedral ZnS_4 core. The two independent Zn-S distances 2.33 and 2.27 Å were significantly different from each other. The entire ligand moiety was almost planar with Zn atom lying 0.47 Å out of the plane. The short sulphur to carbon and carbon to

carbon lengths showed extensive delocalization of the double bonds.

(b) Biuret and their sulphur analogues

Monothioibiuret forms complexes of the type, ML_2Cl_2 [89] ($M = Co(II), Ni(II), Cd(II)$ or $Hg(II)$). The ligand behaved as bidentate in nickel (trans-octahedral) and cadmium(tetrahedral) complexes. In tetrahedral complexes of $Co(II)$ and $Hg(II)$, the ligand acted as unidentate. The metal bis(dithioibiureto)-clusters are of interest [90]. $Fe(II)$ complex may be used as the structural model for biological systems. Complexes of $Zn(II), Ni(II), Sn(II)$ & $Cu(II)$ with substituted dithioibiuret ($R = R' = C_2H_5, CH_3, morpholino$) were synthesized [91] which have been used for population control and as insecticides. Complexes of $Ag(I), Cu(I), Ni(II), Pd(II), Hg(II), Fe(III), Zn(II), Cd(II), Cu(II)$ and $Co(II)$ with substituted dithioibiuret have been proposed as fungicides [92,93]. The complexes, $M^{II}(RNHCSNHCSNHR')_2$ (where $M = Zn, Cd, Hg, Co, Ni, Cu, Pd, Sn$) have been found to have tetrahedral configuration. The following structure has been suggested for the $Fe(III)$ complex:



The structure of the Cu(I) complex, $\text{Cu}(\text{S}_2\text{C}_2\text{N}_3\text{H}_4)\text{Cl}_2$ was determined by X-ray method [94] which was described as an infinite chain of chlorine bridged Cu(I) species and the ligand was bonded to Cu(I) by nitrogen and not through sulphur. Square planar complexes of rhodium and platinum have been prepared [95] and they have the general formula: $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{L}]$, $[\text{Rh}(\text{PPh}_3)_2\text{L}]$, $[\text{PtH}(\text{PPh}_3)\text{L}]$ ($\text{L} = \text{NH}_2\text{CSNHCSNH}_2$, a bidentate coordinating through sulphur atoms).

(c) Pyrrole derivatives as ligands

A study of metal complexes of monothio- β -diketone type of ligands, N-ethoxycarbonylpyrrole-2-thiocarboxamide (ETH) and N-phenylcarbamoypyrrole-2-thiocarboxamide (PTH) was carried out [96] to correlate the different physicochemical properties of the various metal complexes. These ligands can function either as neutral or as anions with nitrogen, sulphur and oxygen as potential donors. Obviously their simultaneous participation in complex formation would virtually be impossible. Thus, monomeric and polymeric forms of complexes have been suggested to form with the metal ions: Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Cd(II), Pt(II), Pt(IV), Pd(II), Rh(I), Rh(III), Ru(II), Ru(III) and Au(III).

The rare occurrence of Co(II) diamagnetic complexes with the pyrrole derivatives as ligands have been explained by the possible formation of δ -bond between two Co(II) ions present in the square planar geometry. Different modes of bonding with

these ligands have been reported: the ligand as bidentate and bonded through thiocarbonyl sulphur and carbonyl oxygen; acting as unidentate and bonded through thioketo sulphur; anionic and neutral forms of the ligand; acting as bidentate towards two metal ions through nitrogen and sulphur atoms or both through nitrogen atoms.

In view of the potential interest in the complexing properties of the above mentioned ligands, having sulphur and nitrogen as donor atoms, it is curious that relatively few transition metal complexes of pyrrole containing ligands have been prepared and studied [97-99] in any detail. Hence with this objective under consideration, the complexes of pyrrole-1,2-dithiodicarbamide as the ligand have been studied with various metal ions. These have been described in Chapter II.

B. Complexes of Ligands analogous to Ethyl N-Phenyldithiocarbamate

The increasing current interest in metal complexes of dithiocarbamate stems from their novel structural [100] and electrochemical properties [101,102] and more recently from their photoredox chemistry [103,104]. In addition, metal dithiocarbamate complexes have been shown to be effective accelerators in the vulcanization of rubber [105]. The investigations on the complexes of dithiocarbamate esters are, however, scanty. The complexes of S-methyldithiocarbamate, S-methyl-N-methyldithiocarbamate and S-methyl-N,N-dimethyldithiocarbamate with Cd(II),

Cu(II) and Hg(II) ions have recently been reported [106].

The chemistry of the coinage metal dithiocarbamate complexes has been studied in considerable detail but only a few reports of dithioaliphatic acid complexes have appeared in the literature. The disubstituted dithiocarbamate Cu(I) complexes are less stable and their solutions oxidise to the corresponding cupric complexes [107]. Since trimers as well as higher polymers were found [108], it appears that the size and structural characteristics of the alkyl chains on the ligands play an important role in determining the degree of polymerization. A variety of $\text{Cu}(\text{R}_2\text{Dtc})_2$ (Dtc = dithiocarbamate) complexes have been prepared and their chemical and magnetic properties have been discussed [109] to support the monomeric nature in solution. The quantitative reactions of Cu(II) with the $\text{Pb}(\text{R}_2\text{Dtc})_2$, $\text{Bi}(\text{R}_2\text{Dtc})_3$ and $\text{Tl}(\text{R}_2\text{Dtc})_3$ complexes to form the deep red-brown, $\text{Cu}(\text{R}_2\text{Dtc})_2$ complex have been used for the indirect determinations of Pb(II), Bi(III) and Tl(III) ions [110]. Further, since Cu(II) ion was able to displace R_2Dtc^- from the $\text{Ni}(\text{R}_2\text{Dtc})_2$, $\text{Zn}(\text{R}_2\text{Dtc})_2$ and $\text{Co}(\text{R}_2\text{Dtc})_3$ complexes, the kinetics of these exchange reactions in acetone have been studied [111]. As a result of the study of the thermal analysis of the $\text{Ni}(\text{R}_2\text{Dtc})_2$ - $\text{Cu}(\text{R}_2\text{Dtc})_2$ system, it has been demonstrated that these complexes are X-ray isomorphous [112]. This observation is consistent with the fact that the $\text{Cu}(\text{R}_2\text{Dtc})_2$ complexes are monomeric and presumably square planar in solution [109,113]. The dithiocarbamate complexes of Ag(I) and Au(I) have been studied and reported to be in hexameric and

dimeric structures, respectively [107].

The yellow $\text{Zn}(\text{MeDta})_2$ and $\text{Cd}(\text{MeDta})_2$, and the unusual $\text{Zn}(\text{MeDTa})\text{ZnS}$ (where MeDta = methyldithio acid) complexes have been reported [114]. Also the $\text{Zn}(\text{Dtb})_2$ and $\text{Zn}(\text{Dtt})_2$ (where Dtb = dithiobenzoate, Dtt = dithiotoluate) compounds have been isolated and the crystal study of $\text{Zn}(\text{Me}_2\text{Dtc})_2$ shows it to be a dimer [115]. The diethyldithiocarbamate complex which is isomorphous and isostructural to the corresponding $\text{Cd}(\text{II})$ complex is also a dimer; however, in this case the ligands are disposed in a different manner about the 5-coordinate $\text{Zn}(\text{II})$ atom [116]. The $\text{Zn}(\text{Et}_2\text{Dtc})_2$ complex was found to be isomorphous to the $\text{Cu}(\text{Et}_2\text{Dtc})_2$ complex [117], although the structural details are different [118].

Though the mercurous and mercuric derivatives of the dithioaliphatic or dithioaromatic acids have been reported, their chemistries are not known in any detail. Dithiocarbamates of $\text{Hg}(\text{I})$ and $\text{Hg}(\text{II})$ are very stable and the fact that $\text{Hg}(\text{II})$ displaces $\text{Cu}(\text{II})$ from the strongly coloured $\text{Cu}(\text{Et}_2\text{Dtc})_2$ complex has been used for the indirect colorimetric determination of Hg^{2+} ion [119]. The reaction of HgCl_2 with $(\text{R}_2\text{Dtc})_2$ compounds has been reported to give $\text{ClHg}(\text{R}_2\text{Dtc})$ complexes [120]. The dithiocarbamate $\text{Hg}(\text{S}_2\text{CNEt}_2)_2$ has two forms, one isomorphous with the Zn and Cd analogues, the other a helical polymer [121]. A considerable number of organomercury dithiocarbamate complexes have been reported and used as preservatives for cellulosic materials [122].

The light yellow compound, $\text{Mn}(\text{Et}_2\text{Dtc})_2$ was found to be X-ray isomorphous to $\text{Cr}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ dithiocarbamates [123]. Dark violet $\text{Mn}(\text{III})$ dithiocarbamates, $\text{Mn}(\text{R}_2\text{Dtc})_3$ ($\text{R} = i\text{-Bu}$, benzyl, piperidine) have been isolated [124]. These are reported to be unstable and slowly decompose to the corresponding $\text{Mn}^{\text{IV}}(\text{R}_2\text{Dtc})_4$ complexes [125]. Single crystal X-ray structural determination of $\text{Mn}(\text{III})$ dithiocarbamate complex has recently been reported [126].

The dithio complexes of $\text{Fe}(\text{II})$ are unstable and quickly air-oxidised to the corresponding $\text{Fe}(\text{III})$ compounds. The $\text{Fe}(i\text{-Bu}_2\text{Dtc})$ complex was prepared and its monomeric nature was supported by cryoscopic measurements in benzene [127]. It was noted that the dithio acid- $\text{Fe}(\text{III})$ complexes were low spin, while the monosubstituted dithiocarbamate complexes were high spin. Cambi et al. [128] recognised for the first time, the possibility of polar resonance forms of the type $\text{R}_2\text{N}^+=\text{C}\begin{smallmatrix} \text{S}^- \\ \text{S}^- \end{smallmatrix}$ in the dithiocarbamates and suggested that they are predominant in the high spin complexes. This explanation finds some justification, since an increase of the effective negative charge on the sulphur atoms would result in a strong π -antibonding effect and a larger ionic radius for the sulphur atoms. The crystal structure of the $\text{Fe}(n\text{-Bu}_2\text{Dtc})_3$ complex has been reported [126,129] and the FeS_6 frame can best be described as an "intermediate between a trigonal prism and a trigonal antiprism." Interesting complexes of the type, $\text{ClFe}(\text{R}_2\text{Dtc})_2$ have been prepared and their crystal structures have been studied to prove that the chlorine atom occupies the apex of a square pyramid [120,130].

Much less is known about the chemistry of the dithio ligands with ruthenium. The low spin ($\mu_{\text{eff}} = 1.74-1.88$ BM), monomeric $\text{Ru}(\text{R}_2\text{Dtc})_3$ complexes ($\text{R} = \text{Me}, \text{Et}, n\text{-Bu}$) have been prepared [131]. The crystal study of the $\text{Ru}(\text{R}_2\text{Dtc})_3$ complexes has shown [132] the $\text{Ru}(\text{III})$ ion to be at the centre of a distorted octahedron defined by the six sulphur atoms. The photochemistry of $\text{Ru}(\text{R}_2\text{Dtc})_3$ ($\text{R} = \text{Me}$ or Et) in chloroform has recently been investigated and the novel chlorine abstraction is reported to give $\text{RuCl}(\text{R}_2\text{Dtc})_3$ [104].

The $\text{Co}(\text{R}_2\text{Dtc})_3$ complexes are reported to be very inert for substitution [133]. The crystal structure of this complex was found to be trigonally distorted octahedral molecule [134]. The red, diamagnetic, water insoluble $\text{Rh}(\text{R}_2\text{Dtc})_3$ complexes with $\text{R} = \text{Me}, \text{Et}$ and $n\text{-Bu}$ have been prepared [131b]. The red-brown $\text{Rh}(\text{Dtb})_3$, the orange $\text{Rh}(\text{BzDta})_3$ and $[\text{Rh}(\text{Dtb})_2\text{Cl}_2]^-$ complexes (where $\text{Dtb} = \text{dithiobenzoate}$, $\text{Dta} = \text{dithio acid}$) were prepared and their electronic spectra have been studied [135]. Recent reports quote some interesting dimeric cationic metal dithiocarbamate complexes with the stoichiometry $\text{M}_2(\text{R}_2\text{Dtc})_5^+$ (where $\text{M} = \text{Ru}(\text{III}), \text{Co}(\text{III})$ and $\text{Rh}(\text{III})$) [136].

A great number of $\text{Ni}(\text{II})$ dithiocarbamates of the type $\text{Ni}(\text{R}_2\text{Dtc})_2$ have been reported and characterized [127,137]. These complexes are neutral, water-insoluble species and their electronic spectra [138], infrared spectra [139] and magnetic properties [140] have been investigated in detail. By X-ray structural

study on the Ni(II) dithiocarbamate complexes a square planar structure of the complexes has been suggested [141]. The structure is strictly planar with the metal, forming a four-membered ring with the carbon disulphide moiety of the ligand. Considerably less is known about the chemistry of palladium and platinum complexes. The $\text{Pt}(\text{i-Bu}_2\text{Dtc})_2$, $\text{Pt}(\text{H}_2\text{Dtc})_2$ and $\text{Pt}(\text{R}_2\text{Dtc})_2$ complexes have been synthesized [127,139d]. The crystal structure of the $\text{Pt}(\text{Et}_2\text{Dtc})_2$ complex has been reported to be very similar to the analogous planar Ni(II) complex [142]. The yellow, diamagnetic, water-insoluble $\text{Pd}(\text{R}_2\text{Dtc})_2$ complexes were prepared and their solubilities in organic solvents increased as the size of the alkyl groups increased [131b]. Having seen the dithiocarbamate complexes, in general, the complexes of ethyl N-phenyldithiocarbamate with various metal ions are detailed in Chapter III.

Although N-sulphinyl group has been known in the form of organic sulphinylamines, covalent and ionic derivatives of other elements have been known only recently. This class of compounds have a pair of terminal cumulated unsaturated groups and can take part in a number of reactions in common. For example, addition reactions are known exclusively to the terminal unsaturated group. The fourth chapter of the thesis describes the syntheses and structural aspects of the complexes of N-sulphinylaniline (NSA) with certain metal salts and metal complexes.

The complexing properties of sulphur monoxide are scarcely known because of its short life time. Despite the instability

of the lower oxides of sulphur, SO , $(\text{SO})_2$ and S_2O all can be trapped as ligands. Using stilbene episulphoxide as the source of SO in dichloromethane, complexes of rhodium(I) with SO are described in the fifth chapter.

The summary of the present work and the scope to continue the work further have been the subject of the sixth chapter.

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CHAPTER II

CHAPTER II

COMPLEXES OF PYRROLE-1,2-DITHIO-
DICARBOXIMIDE WITH Fe(II), Co(I),
Ni(0), Cu(I), Ag(I), Ru(II), Rh(I),
Pd(0) and Pt(0)

A recent interest is to study the complexing behaviour of pyrrole derivatives with various metal ions to get some insight of certain metal chelates in the biological system. This chapter describes the syntheses of the complexes of pyrrole-1,2-dithio-dicarboximide with Fe(II), Co(I), Ni(0), Cu(I), Ag(I), Ru(II), Rh(I), Pd(0) and Pt(0). The stoichiometries and structures of these complexes have been proposed on the basis of analytical, magnetic and spectroscopic (infrared, ultraviolet and visible) studies.

EXPERIMENTAL

All the chemicals used were either chemically pure or of Analar grade. The solvents were dried and freshly distilled before use.

Pyrrole-1,2-dithiodicarboximide (PDD) and the starting complexes: Dichlorobis(triphenylphosphine)iron(II), Dichlorotris(triphenylphosphine)ruthenium(II), Trichlorobis(triphenylarsine)methanol ruthenium(III), Hydridotetrakis(triphenylphosphite)cobalt(I), Chlorotris(triphenylphosphine)rhodium(I), Chlorocarbonylbis(triphenylphosphine)rhodium(I), Tetrakis(triphenylphosphite)nickel(0), Tetrakis(triphenylphosphine)palladium(0), Tetrakis(triphenylphosphine)platinum(0), Chlorotris(triphenylphosphine)copper(I) and Tetrakis(triphenylphosphine)silver(I) nitrate were prepared according to the methods described in the literature [1-11].

Preparation of Metal Complexes

(1) Dichloro(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphine)iron(II)

0.6 g of $[\text{Fe}(\text{PPh}_3)_2\text{Cl}_2]$ (~ 1 mmole) was dissolved in benzene (15 ml) followed by slow addition of PDD (0.4 g, ~ 2 mmole) in benzene (10 ml). The red solution was refluxed for an hour, whereby the colour of the solution was changed to green in the first ten minutes. The clear solution was concentrated to half its original volume under reduced pressure. The greenish brown

complex was precipitated by the addition of 10 ml petroleum ether (60-80°) which was filtered, washed with water, alcohol and ether and dried in vacuum. It was recrystallised twice from benzene-petroleum ether (m.p. 208°) (yield, ~40%).

Anal. Calcd. for $[\text{Fe}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$: C, 61.5; H, 4.1; N, 3.4; S, 7.8; Cl, 8.6; Fe, 6.8. Found: C, 61.0; H, 3.8; N, 3.1; S, 7.6; Cl, 9.1; Fe, 6.8%.

(2) Dichloro(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphine)ruthenium(II)

$[\text{RuCl}_2(\text{PPh}_3)_3]$ (0.5 g, ~0.5 mmole) was dissolved in dry chloroform (15 ml) under nitrogen atmosphere and kept stirred. The ligand, PDD (0.3 g, 1.5 mmole) dissolved in benzene (10 ml) was slowly added. The red-brown solution immediately turned deep blue. The stirring was continued for one more hour and centrifuged. The clear centrifugate was reduced to one-third of its original volume under reduced pressure. About 15 ml of petroleum ether (60-80°) were added to precipitate the blue complex which was filtered, washed with alcohol and ether, and dried under vacuum. It was recrystallised from chloroform-petroleum ether (m.p. 218-219°) (yield, ~48%).

Anal. Calcd. for $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$: C, 58.3; H, 3.9; N, 3.2; S, 7.4; Cl, 8.2; P, 7.2. Found: C, 58.1; H, 3.5; N, 3.2; S, 7.3; Cl, 8.3; P, 7.0%.

(3) Dichloro(pyrrole-1,2-dithiodicarboximide)bis(triphenylarsine)ruthenium(II)

0.4 g (~ 0.5 mmole) of $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ was dissolved in 15 ml of dry chloroform under purified nitrogen atmosphere and kept stirred. A benzene solution (10 ml) of the ligand, PDD (0.34 g, ~ 2 mmole) was slowly added. The red solution turned green. The stirring was continued for one more hour and centrifuged. The clear green solution was evaporated to half of its original volume under reduced pressure, followed by an addition of 10 ml petroleum ether ($60-80^\circ$). On standing for half an hour, a blue precipitate of the complex settled down. It was centrifuged, washed with petroleum ether, n-pentane and dried under vacuum (m.p. $230-232^\circ$) (yield, $\sim 55\%$).

Anal. Calcd. for $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{AsPh}_3)_2]$: C, 52.9; H, 3.6; N, 2.9; S, 6.7; Cl, 7.5. Found: C, 52.8; H, 3.4; N, 2.8; S, 6.8; Cl, 7.8%.

(4) Hydrido(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphite)cobalt(I)

0.6 g (~ 0.5 mmole) of $\text{CoH}(\text{P}(\text{OPh})_3)_4$ was dissolved in dichloromethane (20 ml). To the constantly stirred solution, the ligand, PDD (0.3 g, ~ 2 mmole) in benzene (8 ml) was slowly added, whereupon a dark brown solution immediately resulted. Stirring of the solution was continued for two more hours and it was then centrifuged. The volume of the red-brown solution was reduced to about 10 ml over a water-bath. Addition of

about 10 ml of petroleum ether (60-80°) to the concentrated solution resulted in to give shining brown crystals. which were centrifuged, washed with petroleum ether and dried under vacuum (m.p. 168-170°) (yield, ~30%).

Anal. Calcd. for $[\text{Co}(\text{PDD})\text{H}(\text{P}(\text{OPh})_3)]$: C, 53.5; H, 3.7; N, 5.2; S, 11.9; Co, 11.0. Found: C, 52.8; H, 3.4, N, 5.3; S, 11.7; Co, 10.8%.

(5) Chloro(pyrrole-1,2-dithiodicarboximide)(triphenylphosphine)-rhodium(I)

An orange solution of $\text{RhCl}(\text{PPh}_3)_3$ (0.3 g, ~0.3 mmole) in benzene (10 ml) was mixed with a solution of the ligand, PDD (0.2 g, ~1 mmole) in 10 ml of benzene. The red-orange solution was refluxed for an hour whereupon its colour darkened. After cooling to room temperature, about 10 ml of petroleum ether (60-80°) were added whereupon a dark brown complex precipitated slowly after about three hours. It was centrifuged, washed with alcohol, ether and dried under vacuum. It was recrystallised twice from benzene-petroleum ether (m.p. >300°) (yield, ~60%).

Anal. Calcd. for $[\text{Rh}(\text{PDD})\text{Cl}(\text{PPh}_3)]$: C, 50.6; H, 3.3; N, 4.9; S, 11.3; Cl, 6.3. Found: C, 50.4; H, 3.1; N, 4.8; S, 11.3; Cl, 6.4%.

(6) Monocarbonylmonochloromono (pyrrole-1,2-dithiodicarboximide)-bis(triphenylphosphine)rhodium(I)

0.35 g (~0.5 mmole) of $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ was dissolved in 12 ml of dry chloroform under nitrogen atmosphere. A red solution

of the ligand, PDD (0.3 g, 1.5 mmole) in benzene (10 ml) was slowly added with constant stirring. Stirring was continued for two more hours and the resulting orange solution was concentrated to about 10 ml under reduced pressure. 10 ml of petroleum ether (40-60°) were added to it and the solution was left for an hour. A yellowish brown precipitate slowly settled down, which was centrifuged, washed with petroleum ether and dried under vacuum. It was recrystallised from benzene-petroleum ether (m.p. 230°) (yield, ~45%).

Anal. Calcd. for $[\text{Rh}(\text{PDD})(\text{CO})\text{Cl}(\text{PPh}_3)_2]$: C, 60.1; H, 4.0; N, 3.3; S, 7.5; Cl, 4.2. Found: C, 59.9; H, 3.8; N, 3.2; S, 7.8; Cl, 4.3%.

(7) Mono(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphite)-nickel(0)

$\text{Ni}(\text{P}(\text{OPh})_3)_4$ (0.7 g, ~0.5 mmole) was dissolved in dichloromethane (15 ml) and kept stirred. A solution of the ligand, PDD (0.3 g, ~1.5 mmole) in chloroform (8 ml) was slowly added and stirring was continued for another 1.5 hours. The brown solution was concentrated over a water bath to about 10 ml. 5 ml of alcohol was added to it and after 3 hours, a brown complex settled down. It was centrifuged, washed with ethanol, ether and dried under vacuum. (m.p. 169-170°) (yield, ~30%).

Anal. Calcd. for $[\text{Ni}(\text{PDD})(\text{P}(\text{OPh})_3)_2]$: C, 59.5; H, 4.0; N, 3.3; S, 7.6; Ni, 7.0. Found: C, 59.3; H, 3.7; N, 3.1; S, 7.7; Ni, 6.8%.

(8) Mono(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphine)palladium(0)

$[\text{Pd}(\text{PPh}_3)_4]$ (0.6 g, ~ 0.5 mmole) was added under dry nitrogen atmosphere to about 10 ml of dry and degassed benzene to get a clear yellow solution. It was stirred, and to this stirred solution, a solution of the ligand, PDD (0.3 g, ~ 1.5 mmole) in 10 ml of benzene was slowly added. Stirring was continued for one more hour. About 15 ml of petroleum ether (60-80 $^\circ$) were added to the resulting brown solution and left for an hour whereby a red-brown complex appeared which was centrifuged, washed with alcohol, ether and dried under vacuum. It was recrystallized from benzene-petroleum ether and kept under vacuum (m.p. 176-177 $^\circ$) (yield, $\sim 65\%$).

Anal. Calcd. for $[\text{Pd}(\text{PDD})(\text{PPh}_3)_2]$: C, 63.2; H, 4.3; N, 3.5; S, 8.0; Pd, 13.3. Found: C, 62.9; H, 4.0; N, 3.3; S, 8.1; Pd, 13.2%.

(9) Mono(pyrrole-1,2-dithiodicarboximide)bis(triphenylphosphine)platinum(0)

The procedure followed to prepare the complex was the same as that given in (8), except that $[\text{Pt}(\text{PPh}_3)_4]$ was taken in the place of $[\text{Pd}(\text{PPh}_3)_4]$. A yellowish brown compound (m.p. 198-200 $^\circ$) was obtained (yield, $\sim 60\%$).

Anal. Calcd. for $[\text{Pt}(\text{PDD})(\text{PPh}_3)_2]$: C, 56.8; H, 3.8; N, 3.2; S, 7.2. Found: C, 56.7; H, 3.5; N, 3.3; S, 7.2%.

(10) Chloro(pyrrole-1,2-dithiodicarboximide)(triphenylphosphine)copper(I)

0.44 g (~ 0.5 mmole) of $[\text{CuCl}(\text{PPh}_3)_3]$ was dissolved in 15 ml of benzene and kept stirred. A solution of the ligand, PDD (0.3 g, 1.5 mmole) in benzene (7 ml) was slowly added and stirring was continued for another hour, whereby a dark brown solution was obtained. It was concentrated to about 10 ml over a water-bath and the complex was precipitated by the addition of about 10 ml petroleum ether ($60-80^\circ$). The white complex was recrystallised twice from benzene-petroleum ether, washed with n-pentane and dried in vacuo (m.p. $192-195^\circ$) (yield, $\sim 42\%$).

Anal. Calcd. for $[\text{Cu}(\text{PDD})\text{Cl}(\text{PPh}_3)]$: C, 54.3; H, 3.6; N, 5.3; S, 12.1; Cl, 6.8; Cu, 12.1. Found: C, 54.5; H, 3.4; N, 5.1; S, 12.2; Cl, 6.9; Cu, 12.0%.

(11) Mono(pyrrole-1,2-dithiodicarboximide)(triphenylphosphine)-silver(I) nitrate

15 ml of an acetonitrile solution of $[\text{Ag}(\text{PPh}_3)_4](\text{NO}_3)$ (0.6 g, ~ 0.5 mmole) was taken under nitrogen atmosphere and kept under stirring. 0.3 g (1.5 mmole) of the ligand, PDD dissolved in 10 ml of benzene was slowly added to it and stirring was continued for one more hour. The resulting red-brown solution was concentrated to about 10 ml under reduced pressure, whereupon a pale brown compound was precipitated by the addition of dry ether, which was filtered, washed with alcohol, ether and dried under vacuum. It was recrystallised twice from acetonitrile-ether (m.p. $> 300^\circ$) (yield, $\sim 30\%$).

Anal. Calcd. for $[\text{Ag}(\text{PDD})(\text{PPh}_3)]\text{NO}_3$: C, 48.0; H, 3.2; N, 7.0; S, 10.7; Ag, 18.0. Found: C, 48.2; H, 3.2; N, 7.1; S, 10.5; Ag, 17.7%.

Analyses

An accurately weighed amount of the complex under analysis was decomposed by digesting it in aqua-regia for sometime and evaporating it to near dryness. The semi-solid residue was taken in dilute mineral acids and filtered. The clear filtrate was used for the estimation of the metal ions.

Nickel and palladium were estimated by precipitating them with dimethylglyoxime [12]; copper as copper(I) thiocyanate [12a]; iron as iron(III) oxide [12b] and cobalt as cobalt sulphate [12c]. For the estimation of silver, sulphur and halide, the complex was decomposed by fusing the weighed amount of the complex with KNO_3 and KOH (8 and 64 times, respectively) in a nickel crucible for about 10 minutes. After cooling the melt, it was extracted with distilled water, filtered and the clear filtrate was used to precipitate silver as silver chloride, sulphur as barium sulphate and the halide as silver halide.

Carbon, hydrogen and nitrogen analyses were performed by Microanalytical Section of the Indian Institute of Technology, Kanpur, India. The analytical results are given in the text itself.

Infrared Spectra

Infrared spectra of the ligand and metal complexes were recorded with a Perkin-Elmer 580 diffraction grating spectrophotometer in the range, $4000-250\text{ cm}^{-1}$. Samples were examined as KBr pellets. The major bands of the ligand and complexes are given in Table II.1.

Magnetic Susceptibility Measurements

Magnetic susceptibilities of the complexes were determined with the help of a Gouy balance at room temperature. Mercury-tetrathiocyanatocobalt(II) was used as a magnetic susceptibility standard and the magnetic corrections were estimated by the method outlined by Figgis and Lewis [13]. The results are collected in the Table II.2.

Electronic Spectra

The absorption spectra of the ligand and complexes were measured in chloroform with Cary model 17-D spectrophotometer between 300 and 950 nm. The results are tabulated in the Table II.2.

Melting Points

Melting points of the studied complexes were recorded on a Fisher-Johns melting point apparatus and reported in the text.

Conductivity Measurements

Conductivity measurements of the compounds were made on an Elico conductivity meter type CM-80 of millimolar solutions in nitrobenzene. All the complexes were found to be non-ionic.

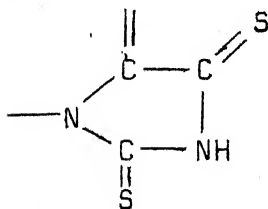
RESULTS AND DISCUSSION

The analytical data suggest that if we assume the metal ions to take up their normally preferred geometries, the ligand is functioning as bidentate towards metal ions in all the complexes except silver and rhodium(I) complexes, where it is acting as monodentate. As a bidentate or a monodentate, it can link with metal ions through any two or one of the three donor atoms viz., the imido-N and the two thiocarbonyl sulphur atoms. The infrared spectra of the ligand and its complexes have been taken to know the possible modes of linkages in the complexes. The major positions of the i.r. bands present in the spectra of the ligand and complexes are given in Table II.1. Based on the comparative i.r. spectral studies of a number of related compounds given in the literature [1], we have tentatively assigned the bands for these complexes.

The characteristic i.r. bands of pyrrole moiety (2910, 1550, 1470, 1450, 1140, 1040, 995, 750, 520 and 440 cm^{-1}) were present in the spectrum of the ligand [14]. The positions of these bands did not shift in the spectra of the complexes (maximum shift $\pm 5\text{ cm}^{-1}$) indicating the non-involvement of

any atom of the pyrrole ring in the bond formation. It also supports the fact that the pyrrole-N atom is poorly basic due to its lone pair of electrons involving for the aromatic sextet and its bridging position is not favourable for bonding. It is, therefore, assumed that bonding in these complexes can take place through $-C(S)NHC(S)-$ moiety of the ligand and the shifts in the positions of the bands are expected to be in the thioimide bands. The major shifts in the band positions arising due to this moiety along with the discussions are as follows:

(a) A broad band (half-width, 100 cm^{-1}) at 3150 cm^{-1} appeared in the spectrum of the ligand. It was assigned to the stretching mode of the NH group. Its broadness could be due to the hydrogen-bonding in the solid state. In the complexed state, the band becomes relatively sharp and its position was shifted to 3060 cm^{-1} . The position of the band of $\nu(\text{NH})$ is considerably lower than that found in other amines, which may be due to the higher electronegativity of the ring,



Further, the shifting of the position of the $\nu(\text{NH})$ band towards lower wave numbers suggested the increased electronegativity of the ring on complexation. In addition, the presence of this band in all the complexes indicated the absence of deprotonation in the complexes.

(b) The infrared spectra of the ligand as well as those of the complexes did not exhibit any band in the $2600\text{--}2000\text{ cm}^{-1}$ region. This suggested that the ligand is present in the thione form at room temperature.

(c) There appeared four bands (1460 cm^{-1} , 1410 cm^{-1} , 1370 cm^{-1} and 1350 cm^{-1}) beside the characteristic bands of pyrrole, in the $1600\text{--}1300\text{ cm}^{-1}$ region, in the spectrum of the ligand. These bands have been assigned to the thioamide bands I and II, which arise due to coupled vibrations of $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$. In the spectra of the complexes, the positions of all these bands shifted towards higher wave numbers. However, the shift in the position of 1460 cm^{-1} band was found to be relatively lesser ($\sim 10\text{ cm}^{-1}$) than those in the other bands ($\sim +25\text{ cm}^{-1}$). The shift in the positions of these bands suggested the interaction of the thioamide groups with the metal ions, whereby the percentage contributions of the various internal coordinates [$\delta(\text{NH})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{C})$] in the normal coordinates giving rise to these bands in the spectrum of the ligand are disturbed and in the spectra of the complexes, new bands due to the normal coordinate having different contributions of the internal coordinates from those of the ligands appear. Since NH group is not participating in the bond formation (vide para (b) above), the shift in the position of the band arising due to normal coordinate having major contribution from $\delta(\text{NH})$, should be relatively small. This has been found for the position of the band at 1460 cm^{-1} . It was, therefore,

assumed that 1460 cm^{-1} band could be assigned to $\delta(\text{NH})$ with minor contribution from $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$. Furthermore, the shifts in the positions of all the four bands in the positive direction suggested the bonding of the metal ions through thio-carbonyl sulphur atom, which will result in the higher bond order of the CN group after complexation. The reason for the presence of four bands in place of the expected two is the presence of two $-\text{N}(\text{H})\text{C}(\text{S})-$ groups in the cis position in ligand molecule which will result in a definite possibility of the interaction of vibrations of these two groups giving rise to four bands.

(d) The spectrum of the ligand showed two broad bands at 1040 cm^{-1} and 820 cm^{-1} . The positions of both the bands shifted towards lower wave numbers ($\sim -20\text{ cm}^{-1}$) in the spectra of the complexes. However, in rhodium and silver complexes, besides the band around 800 cm^{-1} , another new band appeared around 850 cm^{-1} in their spectra. These bands have been assigned to thioamide bands III (having major contribution from the stretching modes of $(\text{C}-\text{C})$, $(\text{C}-\text{N})$ and $(\text{C}=\text{S})$ in the normal coordinate) and thioamide band IV [primarily due to $\nu(\text{C}=\text{S})$], respectively. The shifts in the positions of these bands towards lower wave numbers after complex formation suggested the bonding of metal ion through thiocarbonyl sulphur. Furthermore, it appears that the bonding of the metal ions through thiocarbonyl sulphur atoms resulted in making the two thiocarbonyl groups, in the complexes of rhodium and silver, non-equivalent. It will lead to two

bands due to two kinds of thiocarbonyl groups in their spectra. Thus the thiocarbonyl group, which is bonded to the metal ions, will absorb at relatively lower wave number as compared to the one which is uncomplexed. Therefore, the new band at 850 cm^{-1} in rhodium and silver complexes have been assigned to $\nu(\text{C}=\text{S})$ (uncomplexed). In other complexes, where 850 cm^{-1} band appears could be due to splitting of the 820 cm^{-1} band, one at higher wave numbers [$\sim 850\text{ cm}^{-1}$] and the other at lower wave numbers [$\sim 800\text{ cm}^{-1}$, weak] because of the non-equivalence of two (C=S) moieties.

(e) The position of the band at 490 cm^{-1} in the spectrum of the ligand has been shifted towards lower wave numbers ($\sim -20\text{ cm}^{-1}$) in the spectra of the complexes. This band could be assigned to $\delta(\text{C}=\text{S})$.

(f) One or two new bands appeared around 300 cm^{-1} in the spectra of all the complexes. These bands have been assigned to the coupled vibrations of $\nu(\text{M}-\text{S})$.

(g) The characteristic bands of triphenylphosphine or triphenylarsine were present in the spectra of all the complexes having PPh_3 or AsPh_3 as coligands.

(h) In the spectrum of silver complex, all the characteristic bands of NO_3^- have been found to be present.

It is, therefore, concluded, though tentatively, that the metal ions in all the complexes are bonded to sulphur atoms of the two thiocarbonyl groups. It is hard to distinguish by the

i.r. spectra between monomeric and the polymeric structure of the complexes. But the solubility of the complexes in non-aqueous solvents like dichloromethane, etc. indicated that the degree of polymerization of the complexes cannot be of high order.

Magnetic Moment

All the complexes, except that of Fe(II), are diamagnetic (Table II.2) at room temperature. The diamagnetic nature of $\text{Ru(PDD)Cl}_2(\text{PPh}_3)_2$ and $\text{Ru(PDD)Cl}_2(\text{AsPh}_3)_2$ suggests that ruthenium(II) exists as low spin d^6 system. Since all the known octahedral complexes of ruthenium(II) have been found to be low spin, it is assumed that the complexes, $\text{Ru(PDD)Cl}_2(\text{PPh}_3)_2$ and $\text{Ru(PDD)Cl}_2(\text{AsPh}_3)_2$ have octahedral geometries around ruthenium(II) ions. The diamagnetic behaviour of the complexes, $[\text{Rh(PDD)Cl(PPh}_3)]$, $[\text{Co(PDD)H(P(OPh)}_3)]$ is due to square planar geometry. The other diamagnetic complex, $[\text{Rh(PDD)(CO)Cl(PPh}_3)_2]$ could be assigned to square pyramid or octahedral geometry. The complexes of Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I), which were found to be diamagnetic, belong to d^{10} system. Since d^{10} Ni(0), Pd(0), Pt(0) and Cu(I) complexes are diamagnetic and always form tetrahedral complexes, it is assumed that the geometry of all the complexes under discussion is tetrahedral. Diamagnetic silver complex has been assigned a trigonal or linear geometry. The iron complex has been found to be paramagnetic (5.0 B.M.), corresponding to four unpaired electrons. The ground state of

high spin iron(II), (d^6 system) in octahedral complex is orbitally triply degenerate (${}^5T_{2g}$) and therefore the complex must have higher value of magnetic moment than the spin only value because of definite orbital contribution to the magnetic moment. The value of magnetic moment of the complex, (5.0 B.M.) has been found to be only slightly higher than the spin only value. It may possibly be due to either distortion from the octahedral geometry or it may be due to some experimental error. Generally, high spin iron(II) complexes exhibit a value of magnetic moment larger than 5.2 B.M.

Electronic Spectra

The ultraviolet spectrum of the ligand showed four absorption bands at 390 nm (25641 cm^{-1} , shoulder), 375 nm (26667 cm^{-1}), 255 nm (39216 cm^{-1}) and 235 nm (42553 cm^{-1}). The bands at 390 nm and 375 nm have been assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. The bands at 255 nm and 235 nm are the characteristic bands of substituted pyrrole ring and assigned to $\pi \rightarrow \pi^*$ transitions. These bands did not shift their positions on complexation with the metal ions, meaning thereby that the π - and π^* -energy levels of the ring are not affected. This suggests that the metal ions are not interacting with the π -system of the pyrrole, consistent with the i.r. conclusions. The bands at 390 and 375 nm shifted in their positions on complexation. 375 nm band shifted towards lower wave length ($\sim -10\text{ nm}$), while 390 nm band towards higher wave length

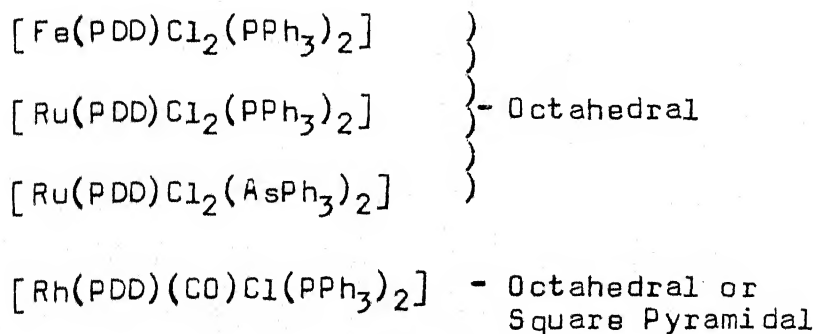
($\sim +20$ nm). In practice, bonding between the thiocarbonyl sulphur and the metal centre ought to stabilize those orbitals having non-bonding electrons, while the π -levels should be destabilized. This effect will show up in the shifts, in the positions of the bands, due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The shifts in the positions of 390 nm towards higher wave length and 375 nm band towards lower wave length indirectly suggested that: (1) 390 nm and 375 nm bands arose due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively and (2) the thiocarbonyl groups of the ligand are interacting with the metal ions in the complexes. In the spectra of all the complexes having PPh_3 , P(OPh)_3 or AsPh_3 , three bands around 285 nm, 275 nm and 265 nm have been observed. These bands are the characteristic bands of the ligands, which may be assigned to $\pi \rightarrow \pi^*$ transition of the phenyl group of the ligands.

The spectra of ruthenium(II) complexes showed two weak bands around 630 nm and 530 nm. One should expect in the spectra of low spin ruthenium(II) complexes, (ground state $^1A_{1g}$) four bands arising due to $^1A_{1g} \rightarrow ^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ transitions. Since the transitions, due to $^1A_{1g} \rightarrow ^3T_{1g}$ and $^3T_{2g}$, will be spin forbidden, the intensities of the bands arising due to these transitions should be very weak ($\epsilon < 10$). The bands around 630 nm and 530 nm have, therefore, been assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1T_{2g}$ respectively. Such bands were observed before in the spectra of analogous complexes of Ru(II) [15].

In the spectra of rhodium(I) complexes, (ground state $^1A_{1g}$) three spin allowed and three spin-forbidden bands are expected. However, only one very weak band around 750 nm (13333 cm^{-1}) was observed owing to the presence of intense charge transfer band in the visible region. This band has been assigned to singlet-singlet transition [16-18].

In the spectra of Ni(0), Pd(0), Pt(0), Cu(I), Ag(I) and high spin Fe(II), no band was observed in the visible region, as expected, because of the fact that these ions belong to d^{10} system. However, in some of the spectra, a weak band was observed around 500 nm, which may be either due to charge transfer ($M \rightarrow L$ or $L \rightarrow M$) or intraligand band.

On the basis of analytical, spectral (ir, uv and visible) and magnetic moment data, it has been concluded that the metal ions are linked with the sulphur atoms and the ligand is acting as bidentate, except rhodium(I) and silver(I) complexes in which it is acting as monodentate. The following tentative geometries have been proposed to the complexes:



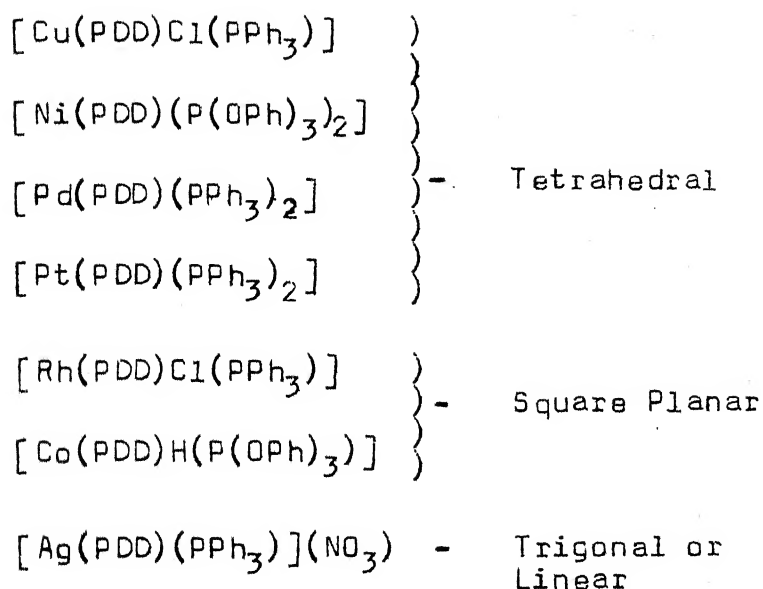


Table II.1

Assignments of Major Infrared Bands of the
Ligand and its Complexes

PDD (cm^{-1})	Complexes (cm^{-1})	Assignments
3150(br)	3060(m)	$\nu(\text{NH})$
1460(br)	1470(± 5)(m)	Thioamide band I $\delta(\text{NH}) + \nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$
1410(s)	1435(± 5)(s)	
1370(m)	1395(± 5)(m)	Thioamide band II $\delta(\text{NH}) + \nu(\text{C}=\text{N})$
1350(m)	1375(± 5)(m)	
1040(m)	~ 1020 (m)	Thioamide band III $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{N}) + \nu(\text{C}=\text{S})$ with major contribution from $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{N})$
820(br)	~ 800 (m)	Thioamide band IV with major contribution from $\nu(\text{C}=\text{S})$
	850(w)	$\nu(\text{C}=\text{S})$ (uncomplexed)
490(w)	470(m)	$\delta(\text{C}=\text{S})$
	~ 300 (m)	One or two bands due to coupled vibrations of $\nu(\text{M}-\text{S})$

(br), broad; (m), medium; (s), strong; (w), weak.

Table II.2

Magnetic Moments Data, Electronic Absorption Band
Positions and Their Assignments

Compound	Band positions nm (cm ⁻¹)	Assignments	Magnetic Moments (B.M.)	
			3	4
PDD	390 (25,641)(sh) 375 (26,667) 255 (39,216) 235 (42,553)	n → π* π → π* Characteristic bands of pyrrole ring and may arise due to π → π* transitions		
All the complexes	410 (24,390) 365 (27,397) 285 (35,088) (±5 nm) 275 (36,364) (±5 nm) 265 (37,736) (±5 nm) 255 (39,216) 235 (42,553)	n → π* π → π* π → π* due to phenyl group in PPh ₃ or P(OPh) ₃		
		Pyrrole ring bands		
[Ru(PDD)Cl ₂ (PPh ₃) ₂]	630 (15,873)(w)	¹ A _{1g} → ¹ T _{1g}		DM
[Ru(PDD)Cl ₂ (AsPh ₃) ₂]	530 (18,868)(w)	¹ A _{1g} → ¹ T _{2g}		DM

..contd.

Table II.2 (contd.)

1	2	3	4
[Rh(PDD)Cl(PPh ₃)]	} 750 (13,333)(vw)	$^1A_{1g} \rightarrow ^1T_{1g} \text{ or } ^1T_{2g}$	DM
[Rh(PDD)(CO)Cl(PPh ₃) ₂]			
[Fe(PDD)Cl ₂ (PPh ₃) ₂]	500 (20,000)(w)	CT or IL	5.0
[Ni(PDD)(P(OPh) ₃) ₂]	-	-	DM
[Pd(PDD)(PPh ₃) ₂]	-	-	DM
[Pt(PDD)(PPh ₃) ₂]	-	-	DM
[Cu(PDD)Cl(PPh ₃)]	-	-	DM
[Ag(PDD)(PPh ₃)](NO ₃)	-	-	DM

DM, diamagnetic; (sh), shoulder; (w), weak; (vw), very weak; CT, charge transfer; IL, intraligand.

LEGEND TO THE FIGURES

Fig. II.1 Infrared Spectra of PDD and Its Complexes:

- (1) PDD
- (2) $[\text{Fe}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$
- (3) $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$
- (4) $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{AsPh}_3)_2]$
- (5) $[\text{Co}(\text{PDD})\text{H}(\text{P}(\text{OPh})_3)]$
- (6) $[\text{Rh}(\text{PDD})\text{Cl}(\text{PPh}_3)]$
- (7) $[\text{Rh}(\text{PDD})(\text{CO})\text{Cl}(\text{PPh}_3)_2]$
- (8) $[\text{Ni}(\text{PDD})(\text{P}(\text{OPh})_3)_2]$
- (9) $[\text{Pd}(\text{PDD})(\text{PPh}_3)_2]$
- (10) $[\text{Pt}(\text{PDD})(\text{PPh}_3)_2]$
- (11) $[\text{Cu}(\text{PDD})\text{Cl}(\text{PPh}_3)]$
- (12) $[\text{Ag}(\text{PDD})(\text{PPh}_3)](\text{NO}_3)$

Fig. II.2 Electronic Spectra of PDD and its Complexes:

- (1) PDD
- (2) $[\text{Fe}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$
- (3) $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{PPh}_3)_2]$
- (4) $[\text{Ru}(\text{PDD})\text{Cl}_2(\text{AsPh}_3)_2]$
- (5) $[\text{Rh}(\text{PDD})\text{Cl}(\text{PPh}_3)]$
- (6) $[\text{Rh}(\text{PDD})(\text{CO})\text{Cl}(\text{PPh}_3)_2]$
- (7) $[\text{Ni}(\text{PDD})(\text{P}(\text{OPh})_3)_2]$
- (8) $[\text{Co}(\text{PDD})\text{H}(\text{P}(\text{OPh})_3)]$
- (9) $[\text{Pd}(\text{PDD})(\text{PPh}_3)_2]$
- (10) $[\text{Cu}(\text{PDD})\text{Cl}(\text{PPh}_3)]$

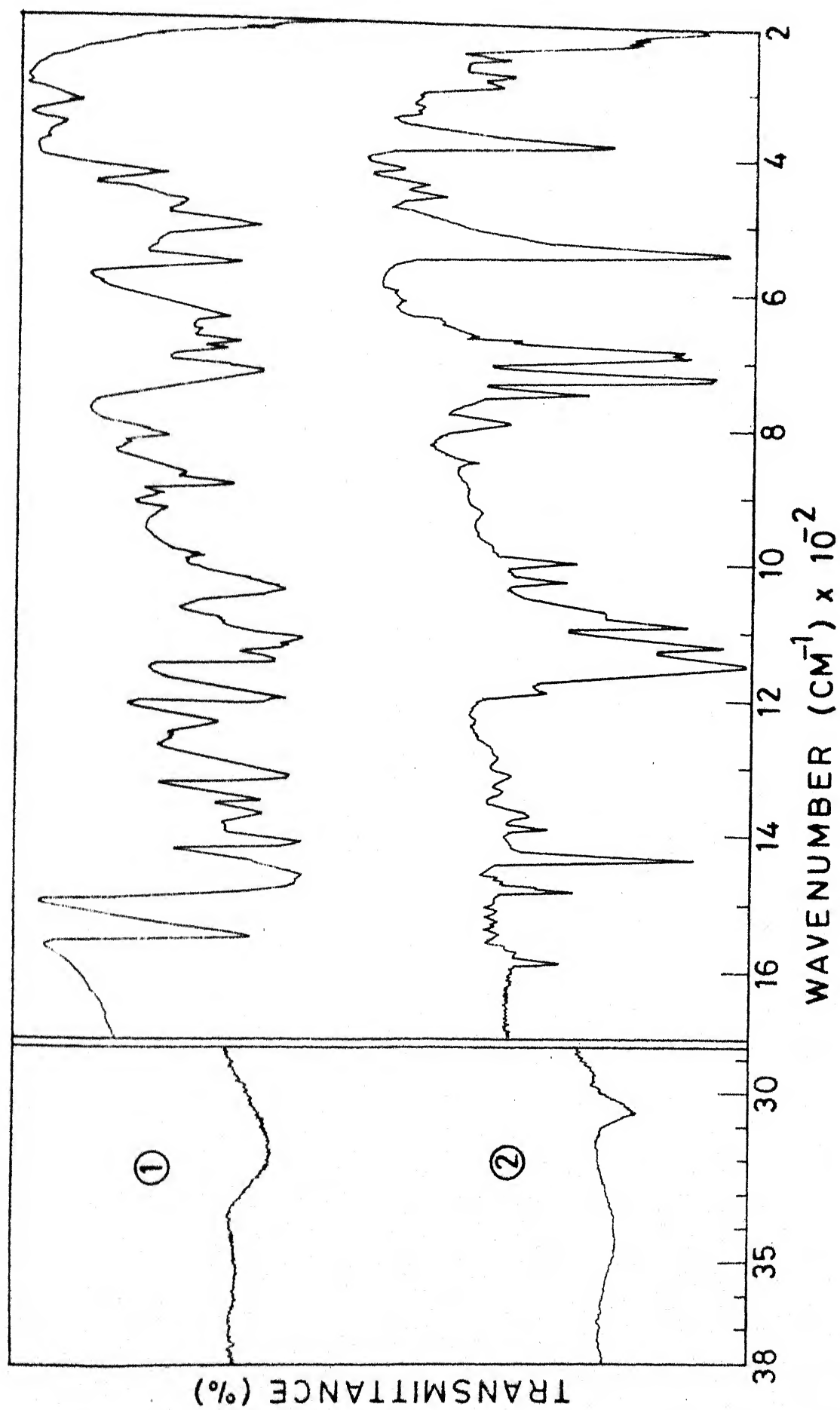


FIG. II.1 INFRARED SPECTRA OF ① & ② .

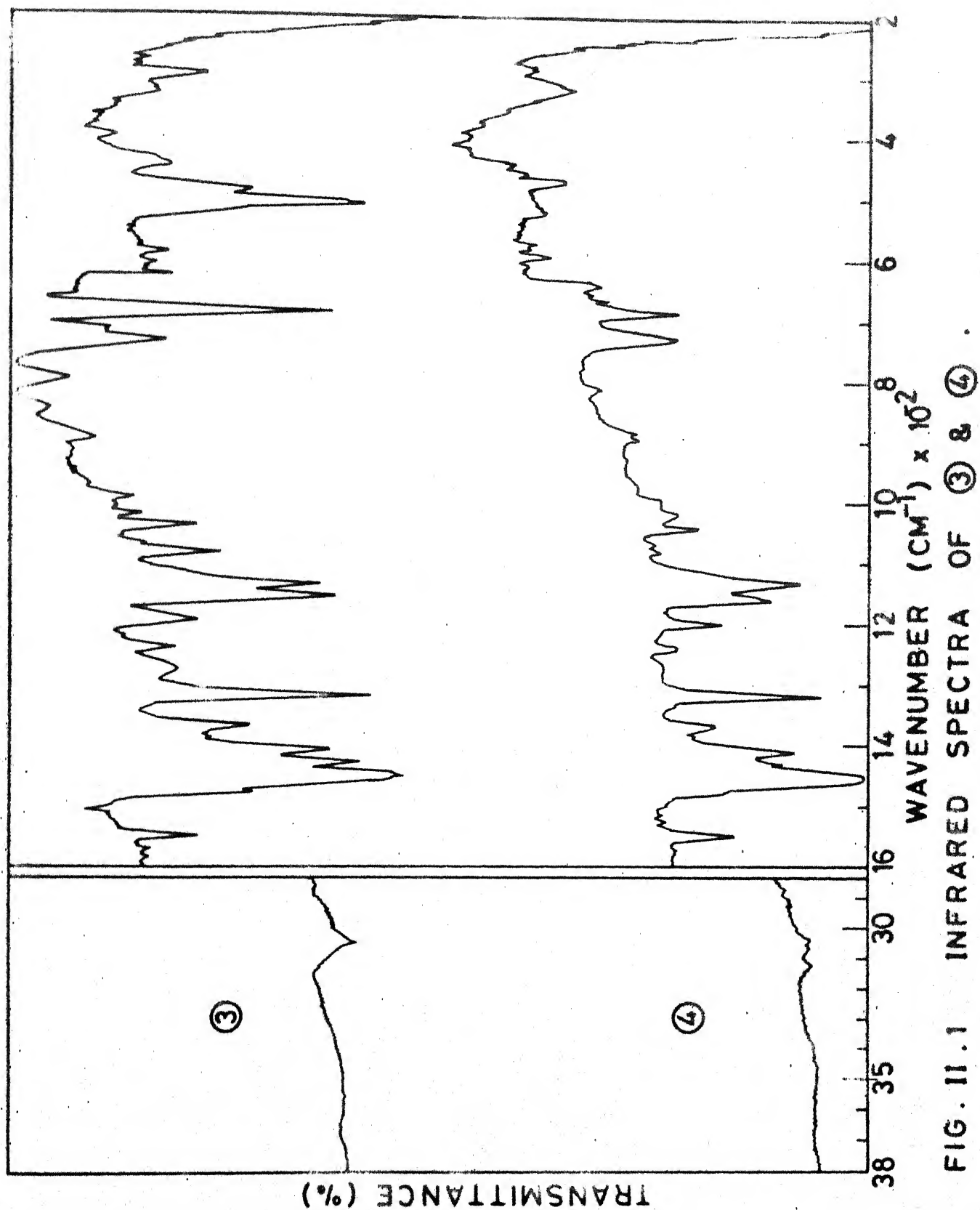


FIG. II.1 INFRARED SPECTRA OF ③ & ④ .

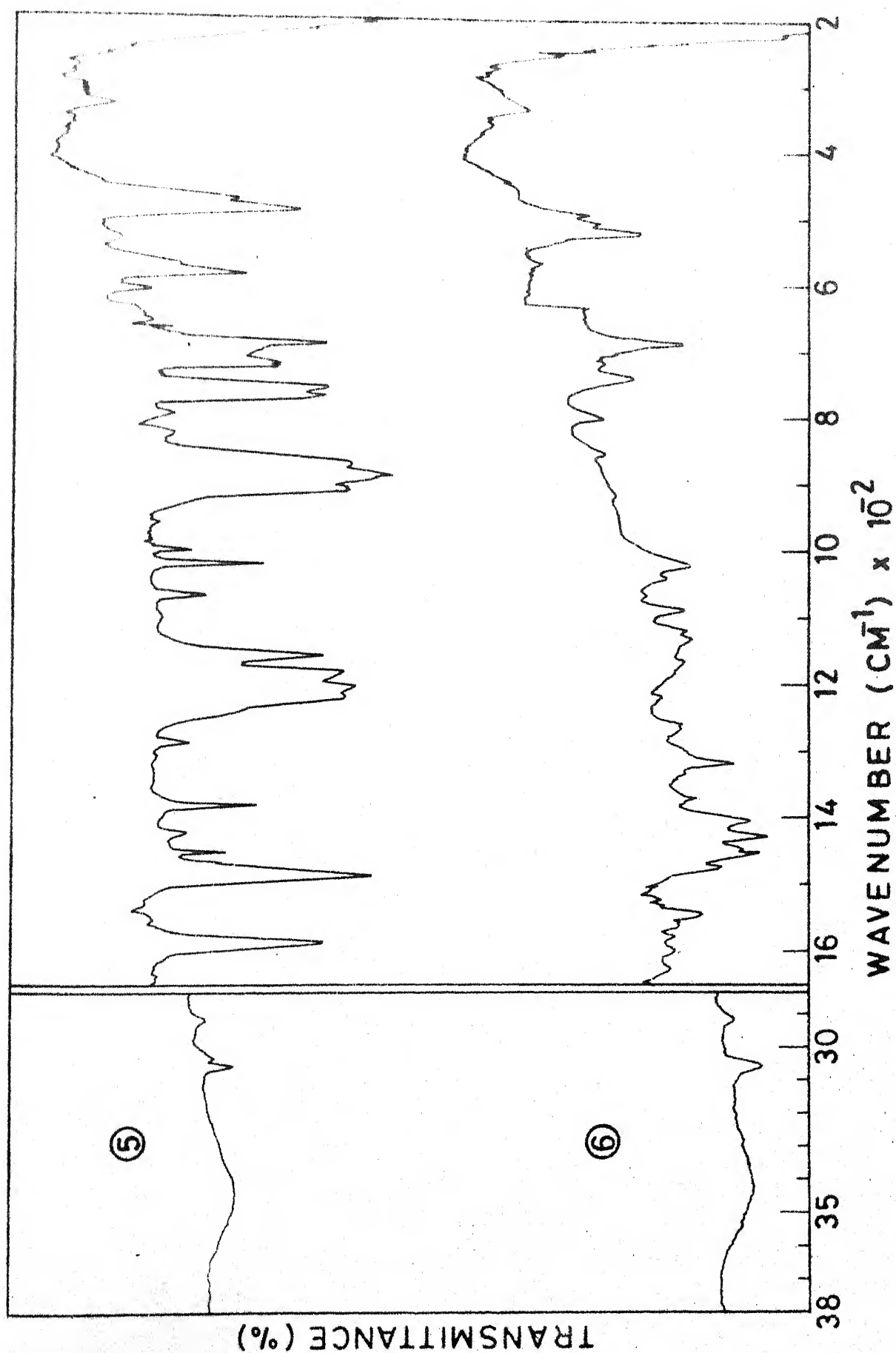


FIG. II.1 INFRARED SPECTRA OF ⑤ & ⑥

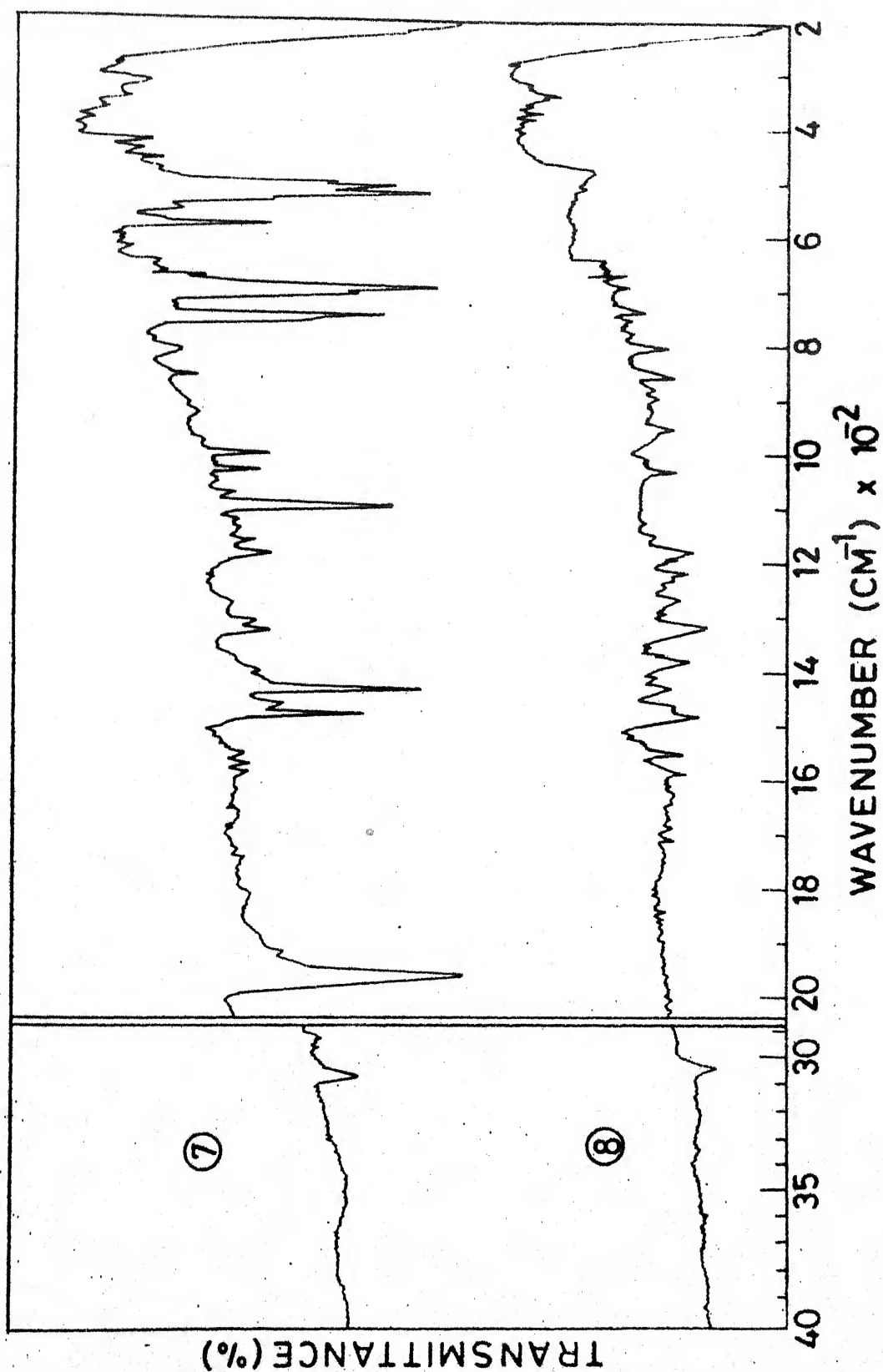


FIG. II.1 INFRARED SPECTRA OF ⑦ & ⑧.

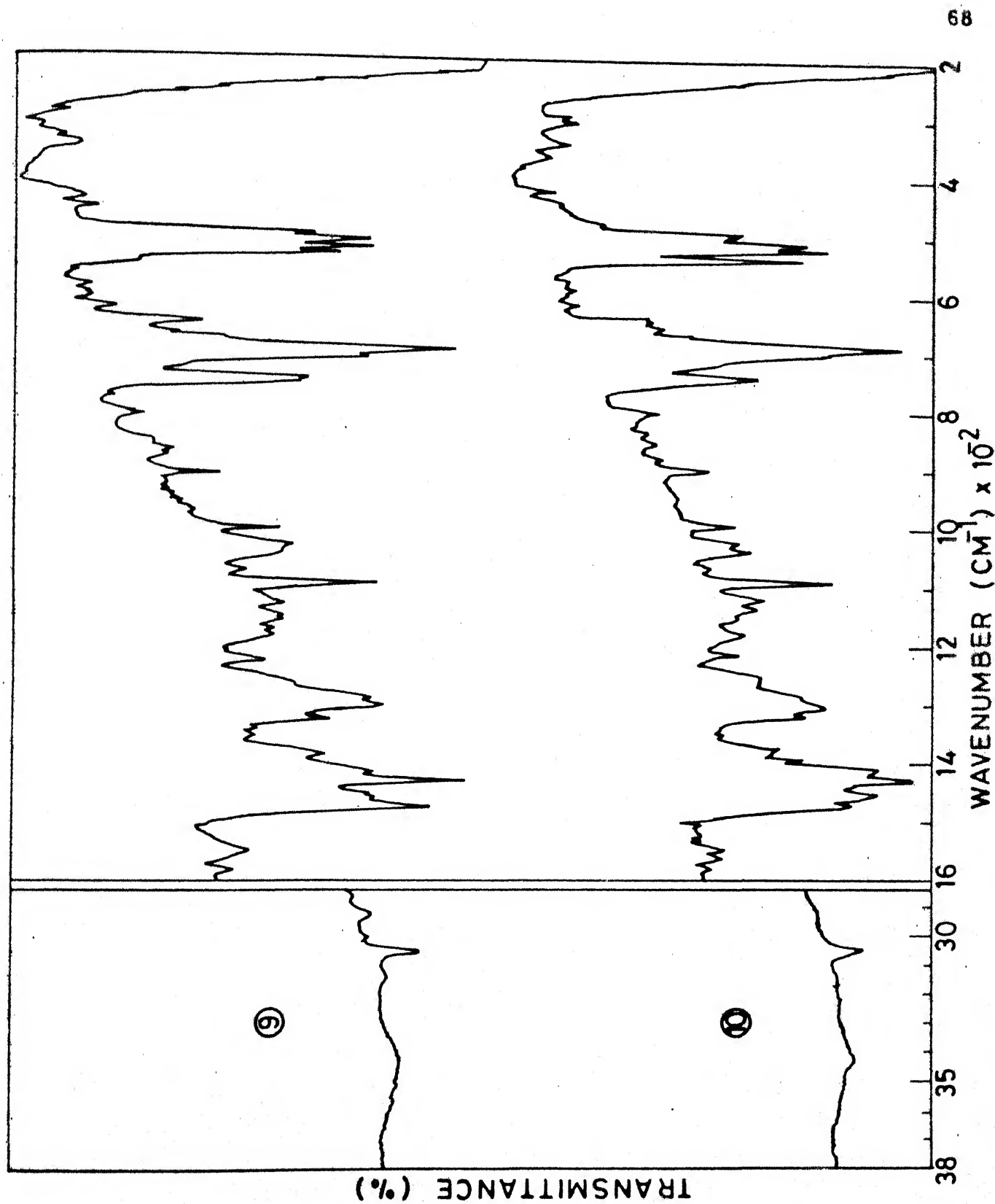


FIG. II.1 INFRARED SPECTRA OF ⑨ & ⑩

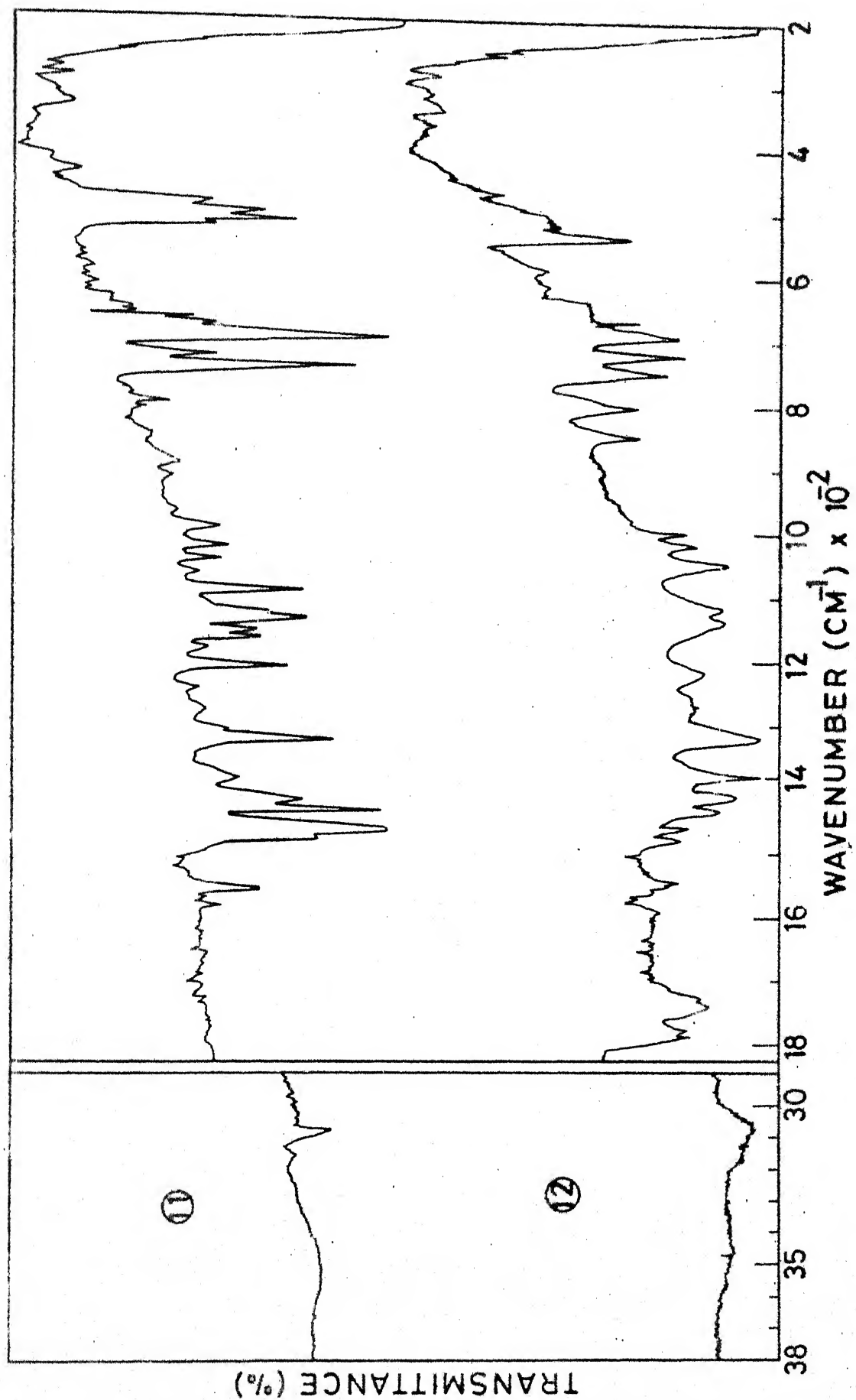


FIG. II.1 INFRARED SPECTRA OF 11 & 12 .

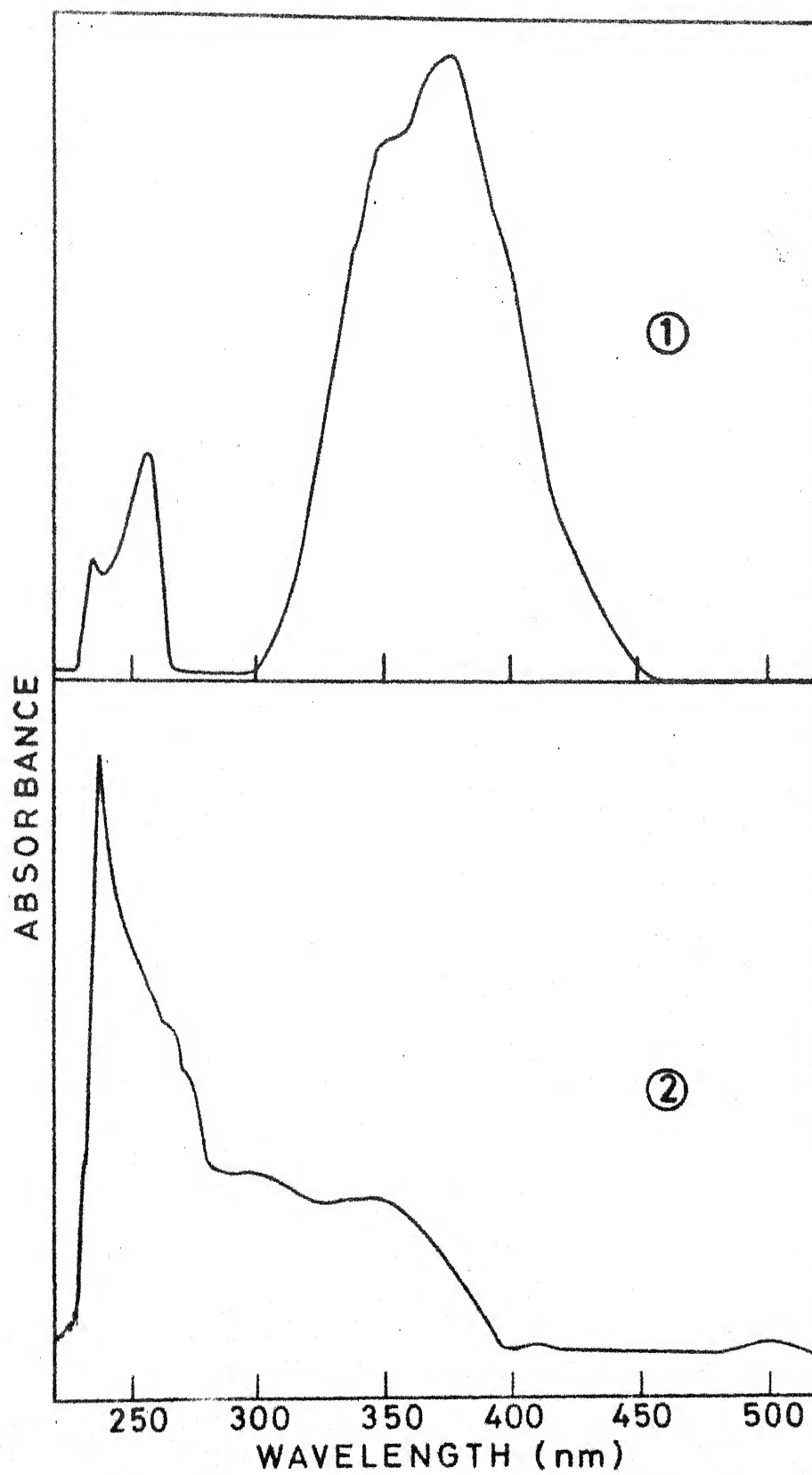


FIG.II.2 ELECTRONIC SPECTRA OF ① & ② .

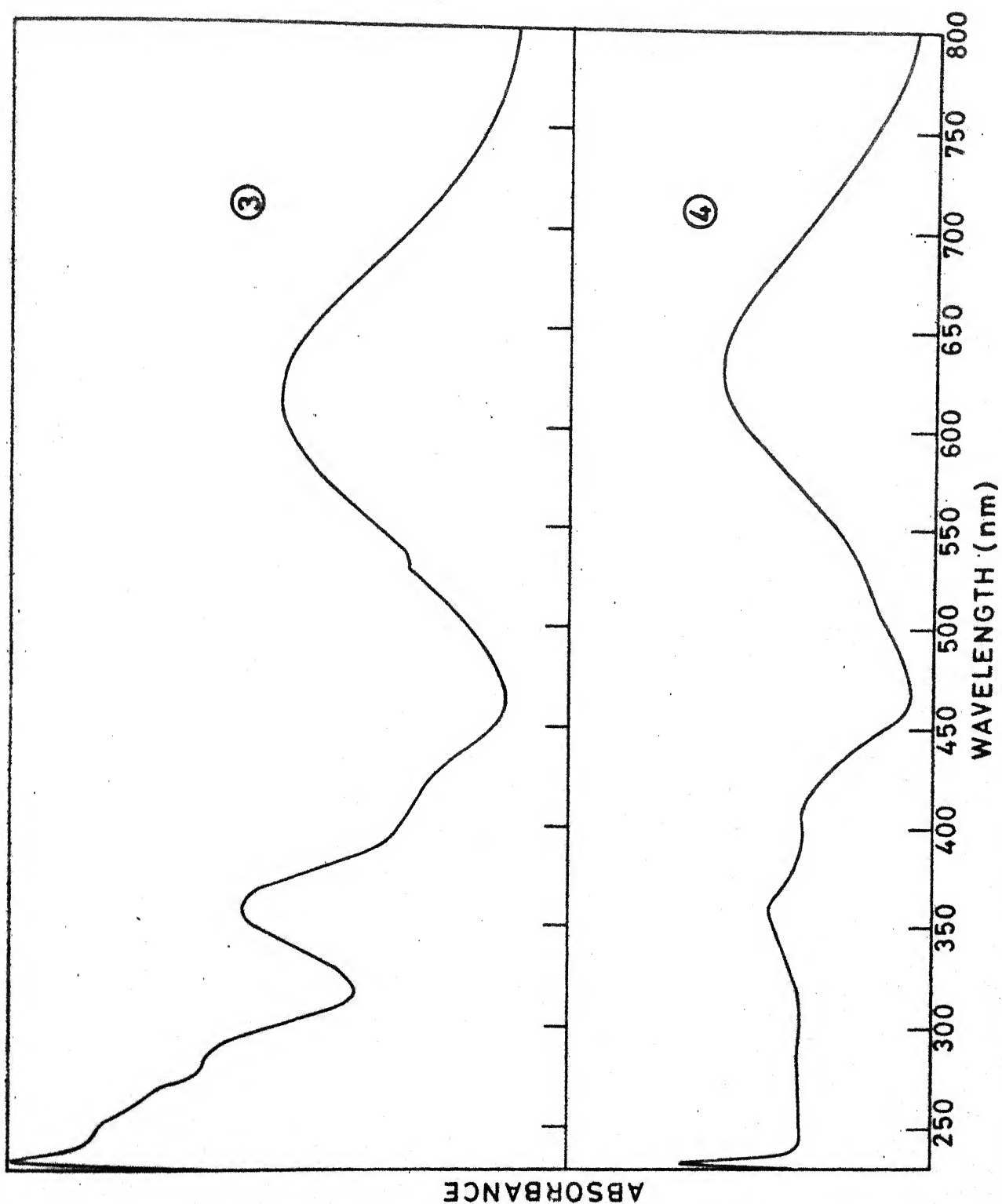


FIG. II.2 ELECTRONIC SPECTRA OF ③ & ④.

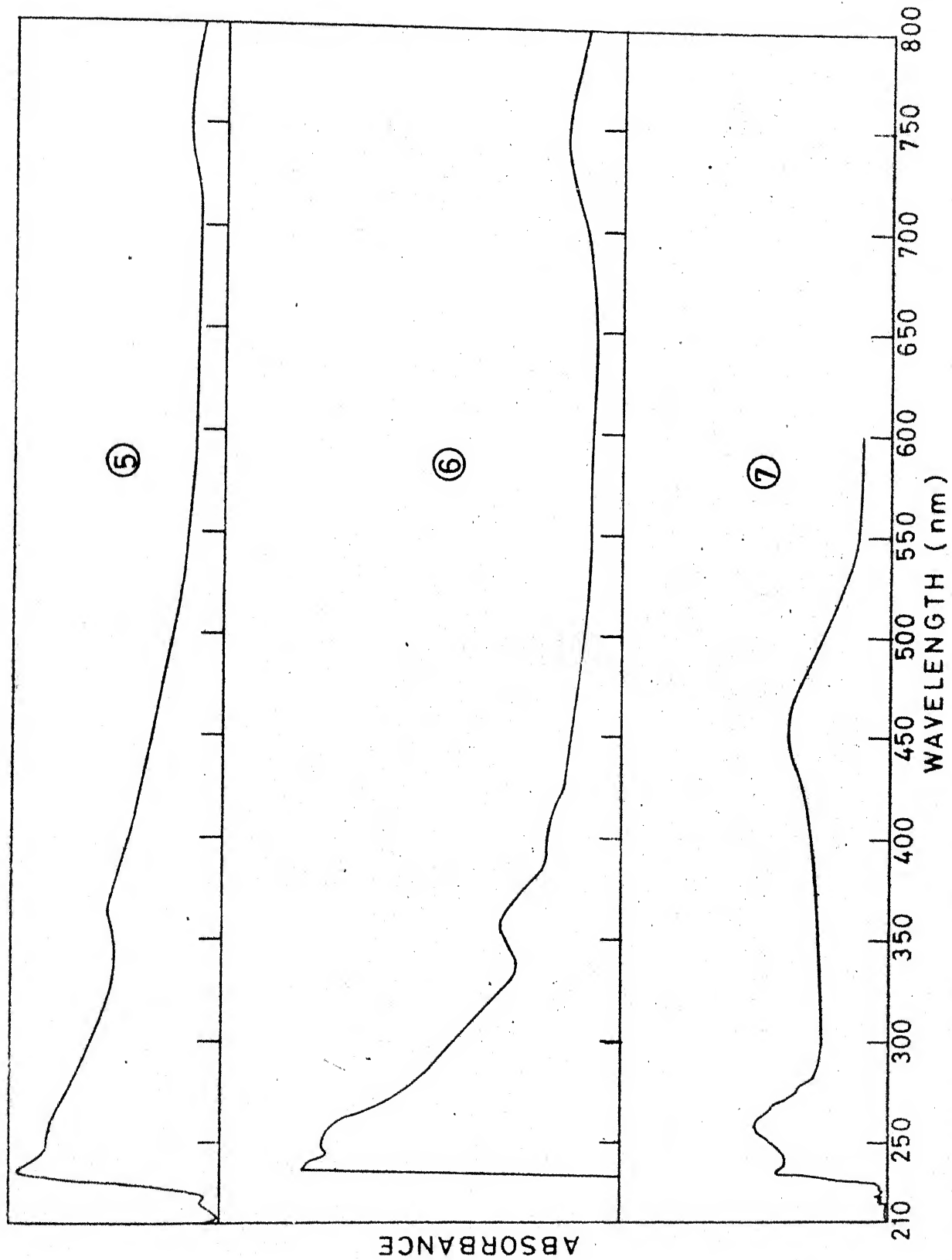


FIG. II.2 ELECTRONIC SPECTRA OF ⑤ ⑥&⑦

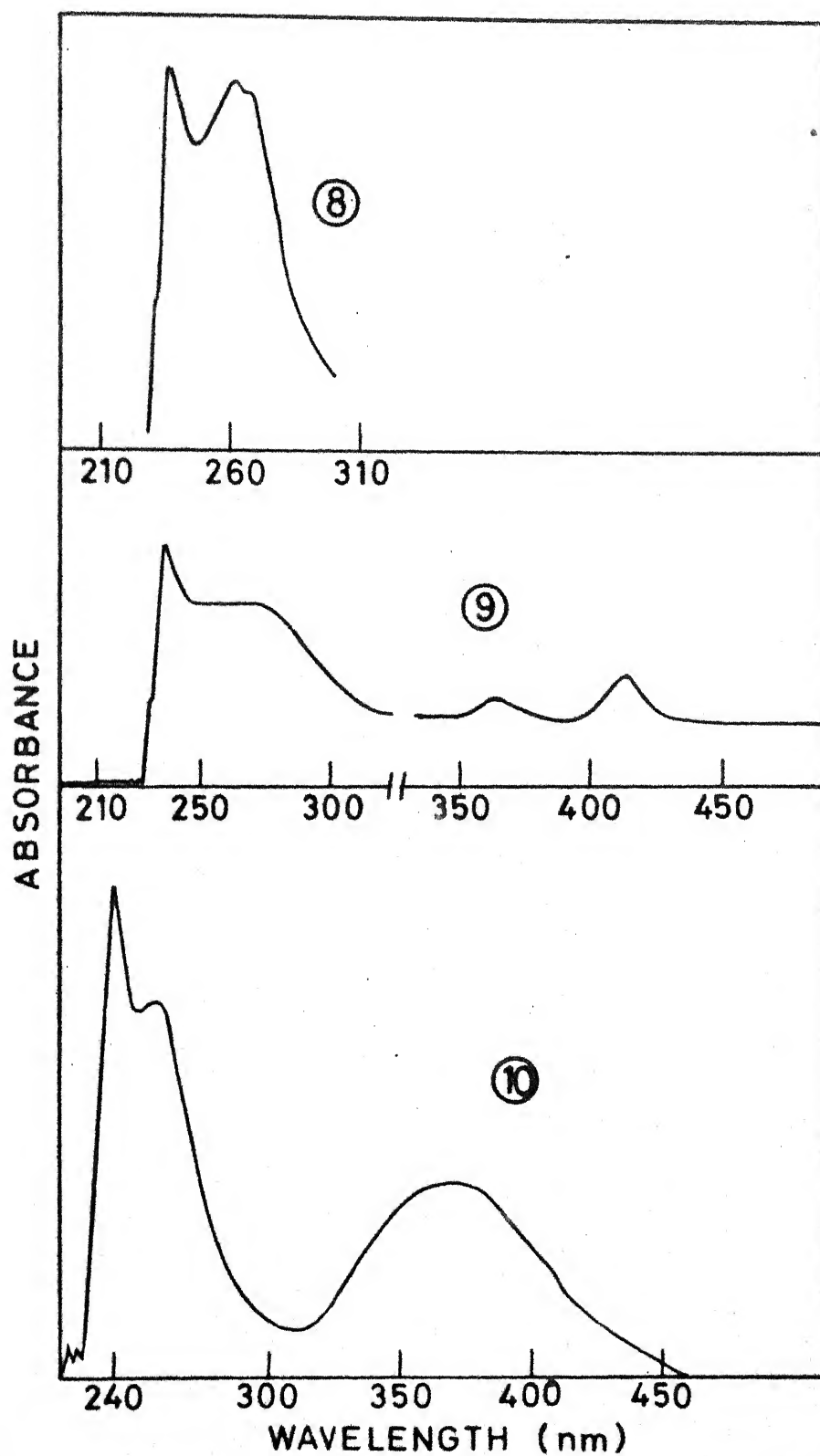


FIG. II.2 ELECTRONIC SPECTRA OF ⑧ ,
⑨ & ⑩

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CHAPTER III

CHAPTER III

COMPLEXING BEHAVIOUR OF ETHYL N-PHENYLDITHIOCARBAMATE: COMPLEXES OF Fe(III), Ru(II), Co(II), Rh(III), Rh(I), Ni(II), Pd(0), Pt(0), Pt(II) AND Ag(I)

This chapter deals with syntheses, analyses, magnetic and spectroscopic (ir, uv and visible) investigation of the complexes of Fe(III), Ru(II), Co(II), Rh(III), Rh(I), Ni(II), Pd(0), Pt(0), Pt(II) and Ag(I) with Ethyl N-phenyldithiocarbamate. The tentative structures of these complexes have been proposed on the basis of the analytical, magnetic and spectroscopic (ir, electronic) data.

EXPERIMENTAL

All the chemicals used were either chemically pure or of Analar grade. The solvents were dried and freshly distilled before use. Ethyl N-phenyldithiocarbamate (hereafter referred to as EPD) was prepared by a known method [1] and used after recrystallization from ethyl alcohol. Chlorotris(triphenylphosphine)rhodium(I), Tetrakis(triphenylphosphine)palladium(0) and Tetrakis(triphenylphosphine)platinum(0) were prepared by reported methods, as in the previous Chapter II.

Preparation of Metal Complexes

(1) Dichlorobis(ethyl N-phenyldithiocarbamate)iron(II)

A benzene solution (15 ml) of anhydrous FeCl_3 (0.32 g, ~ 2 mmole) was added with stirring to a chloroform solution (15 ml) of the ligand (1.6 g, ~ 8 mmole) and stirring was continued for one hour. The resulting dark brown solution was concentrated to about 15 ml under reduced pressure. On addition of petroleum ether (40-60 $^\circ$) to the concentrated solution, a red-brown precipitate of the complex was obtained. It was centrifuged, washed with petroleum ether and recrystallized twice from chloroform-petroleum ether followed by vacuum drying (m.p. 125-127 $^\circ\text{C}$)(yield, $\sim 50\%$).

Anal. Calcd. for $[\text{FeCl}_2(\text{EPD})_2]$: C, 41.5; H, 4.2; N, 5.4; S, 24.6; Cl, 13.6; Fe, 10.8. Found: C, 41.2; H, 4.0; N, 5.2; S, 24.3; Cl, 13.8; Fe, 10.4%.

(2) Dichlorotris(ethyl N-phenyldithiocarbamate)ruthenium(II)

An ethanolic solution (8 ml) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.3 g, ~ 1 mmole) was slowly added to 10 ml of the ligand solution (0.8 g, ~ 4 mmole) in chloroform with constant stirring. After an hour, the red-brown solution was warmed over a water-bath to reduce the volume to about 10 ml and 10 ml of ether was added to it, whereby a dark red complex was precipitated. It was centrifuged, washed with ether and dried in a vacuum desiccator (m.p. $137-138^\circ\text{C}$) (yield, $\sim 58\%$).

Anal. Calcd. for $[\text{RuCl}_2(\text{EPD})_3]$: C, 42.5; H, 4.3; N, 5.5; S, 25.2; Cl, 9.3. Found: C, 41.8; H, 4.1; N, 5.6; S, 24.8; Cl, 9.7%.

(3) Dichlorobis(ethyl N-phenyldithiocarbamate)cobalt(II) ethanol

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 g, ~ 2 mmole) in ethanol (12 ml) was slowly added with stirring to 15 ml of the ligand solution (1.6 g, ~ 8 mmole) in chloroform. The colour of the solution was changed to dark green. Stirring was continued for an hour and the resulting solution was concentrated over a water-bath to about 10 ml. On addition of petroleum ether ($40-60^\circ$) to the solution, a green oil separated out of the solution which was separated by a separating funnel. It was dissolved in chloroform and recrystallized by petroleum ether. The process of recrystallization from chloroform-petroleum ether was repeated several times, whereupon a green complex was separated which was

centrifuged, washed with petroleum ether and dried in air (m.p. 149-151°C)(yield, ~45%).

Anal. Calcd. for $[\text{CoCl}_2(\text{EPD})_2] \cdot \text{C}_2\text{H}_5\text{OH}$: C, 42.1; H, 4.9; N, 4.9; S, 22.5; Cl, 12.5; Co, 10.4. Found: C, 41.8; H, 4.7; N, 5.1; S, 22.8; Cl, 13.1; Co, 9.9%.

(4) Trichlorotris(ethyl N-phenyldithiocarbamate)rhodium(III)

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.26 g, ~1 mmole) dissolved in 10 ml of alcohol was slowly added with stirring to a solution of the ligand (0.8 g, ~4 mmole) in 10 ml of benzene. The solution was stirred at 10°C for about an hour, whereupon the colour of the light brown solution changed to dark brown. On addition of 15 ml of petroleum ether (40-60°), a red-orange complex was precipitated. It was centrifuged, washed with n-pentane and dried in vacuum. It was recrystallised twice from chloroform-petroleum ether followed by washing a few times with n-pentane (m.p. 185-188°C) (yield, ~65%).

Anal. Calcd. for $[\text{RhCl}_3(\text{EPD})_3]$: C, 40.5; H, 4.1; N, 5.2; S, 23.9; Cl, 13.4; Rh, 12.9. Found: C, 40.1; H, 3.9; N, 5.0; S, 23.6; Cl, 13.6; Rh, 12.3%.

(5) Chlorobis(ethyl N-phenyldithiocarbamate)triphenylphosphine-rhodium(I)

Chlorotris(triphenylphosphine)rhodium(I) (0.31 g, 0.33 mmole) was dissolved in 10 ml of chloroform. A yellow solution of the ligand (0.3 g, ~1.5 mmole) in chloroform (10 ml) was slowly

added with stirring under nitrogen atmosphere and stirring was continued for 1.5 hr. From the resulting red-brown solution, a yellowish brown complex was isolated by the addition of petroleum ether (40-60°) which was centrifuged, washed with alcohol, ether and dried under vacuum. It was recrystallized from chloroform-petroleum ether mixture a few times, until a constant melting compound was obtained (m.p. 170-173°C)(yield, ~ 50%).

Anal. Calcd. for $[\text{RhCl}(\text{EPD})_2(\text{PPh}_3)]$: C, 54.3; H, 4.6; N, 3.5; S, 16.1; Cl, 4.5; Rh, 12.9; P, 3.9. Found: C, 53.9; H, 4.4; N, 3.2; S, 16.2; Cl, 4.6; Rh, 12.5; P, 3.6%.

(6) Dichlorobis(ethyl N-phenyldithiocarbamate)nickel(II)

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g, 0.2 mmole) was dissolved in 15 ml of alcohol and slowly added with stirring to the ligand solution (1.6 g, ~8 mmole) in 10 ml of dichloromethane. After having stirred for about an hour, the solution was slowly evaporated to half of its original volume over a water-bath. Addition of ether gave a green oil, which was separated. It was dissolved in dichloromethane and precipitated by dried petroleum ether. This process of recrystallization was repeated three to four times, until a constant melting light green complex was obtained. It was centrifuged, washed with petroleum ether and dried in air, (decomposed at 265-270°C)(yield, ~ 40%).

Anal. Calcd for $[\text{NiCl}_2(\text{EPD})_2]$: C, 41.4; H, 4.2; N, 5.0; S, 24.8; Cl, 13.5; Ni, 11.2. Found: C, 41.1; H, 4.1; N, 5.4; S, 24.5; Cl, 13.8; Ni, 11.1%.

(7) Bis(ethyl N-phenyldithiocarbamate)bis(triphenylphosphine)-palladium(0)

Tetrakis(triphenylphosphine)palladium(0) (0.6 g, ~ 0.5 mmole) was dissolved in 12 ml of benzene under nitrogen atmosphere. To this stirred yellow solution, the ligand (0.5 g, ~ 2.5 mmole) in 10 ml of chloroform was slowly added. Stirring was continued for about three hours whereby the colour of the yellow solution slowly changed to red. The final volume was reduced to half under reduced pressure. The addition of about 15 ml petroleum ether (40-60°) resulted in a red oil which was separated, redissolved in chloroform and precipitated by petroleum ether (40-60°). The process of recrystallization was repeated a few times until a yellow complex having constant melting point was obtained. It was centrifuged, washed with alcohol and ether, dried and kept in a vacuum desiccator (m.p. 124-126°C) (yield, ~ 45%).

Anal. Calcd. for $[\text{Pd}(\text{EPD})_2(\text{PPh}_3)_2]$: C, 63.3; H, 5.1; N, 2.7; S, 12.5; P, 6.1; Pd, 10.3. Found: C, 62.8; H, 4.9; N, 2.6; S, 12.3; P, 5.8; Pd, 10.2%.

(8) Bis(ethyl N-phenyldithiocarbamate)bis(triphenylphosphine)-platinum(0)

The procedure to synthesize the complex was the same as that given in (7) except that tetrakis(triphenylphosphine)-platinum(0) was taken in the place of tetrakis(triphenylphosphine)palladium(0). A pale yellow complex was obtained (m.p. 162-165°C) (yield, ~ 50%).

Anal. Calcd. for $[\text{Pt}(\text{EPD})_2(\text{PPh}_3)_2]$: C, 58.4; H, 4.7; N, 2.2; S, 11.6; P, 5.6. Found: C, 58.1; H, 4.6; N, 2.6; S, 11.3; P, 5.4%.

(9) Dichlorobis(ethyl N-phenyldithiocarbamate)platinum(II)

Platinous chloride (0.3 g, 1 mmole) was dissolved in alcohol (8 ml) and the solution was added with stirring to a chloroform (10 ml) solution of the ligand (0.8 g, 4 mmole). Stirring was continued at room temperature for two hours, whereby a yellow complex was slowly formed. It was centrifuged, washed with petroleum ether and dried in vacuum (m.p. 140-142°C) (yield, ~55%).

Anal. Calcd. for $[\text{PtCl}_2(\text{EPD})_2]$: C, 32.7; H, 3.3; N, 4.0; S, 19.4; Cl, 10.4. Found: C, 32.4; H, 3.1; N, 4.3; S, 19.3; Cl, 10.8%.

(10) Bis(ethyl N-phenyldithiocarbamate)silver(I) nitrate

AgNO_3 (0.34 g, ~2 mmole) dissolved in 20 ml of hot aqueous alcohol was kept under stirring. A chloroform solution (12 ml) of the ligand (1.6 g, ~8 mmole) was slowly added and stirred for 3.5 hr. A dark red complex was slowly formed. It was centrifuged, washed with alcohol, benzene and petroleum ether followed by drying in a vacuum desiccator (m.p. 180-182°C) (yield, ~53%).

Anal. Calcd. for $[\text{Ag}(\text{EPD})_2](\text{NO}_3)$: C, 38.3; H, 3.0; N, 7.5; S, 22.9; Ag, 19.2. Found: C, 37.9; H, 3.5; N, 7.3; S, 22.5; Ag, 19.0%.

(11) Dichlorobis(ethyl N-phenyldithiocarbamate)zinc(II)

An alcoholic solution (10 ml) of $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g, 2 mmole) was stirred with a solution of the ligand (1.6 g, ~ 8 mmole) in chloroform (10 ml) for an hour and subsequently refluxed for half an hour over a water-bath. The light brown solution was cooled and treated with 15 ml of ether whereby a yellow oil was obtained. It was separated, dissolved in chloroform and precipitated by petroleum ether (40-60°). The process of recrystallization was repeated three to four times, whereby a constant melting yellow solid was obtained which was dried in vacuo (m.p. 95-98°C)(yield, $\sim 60\%$).

Anal. Calcd. for $[\text{ZnCl}_2(\text{EPD})_2]$: C, 40.8; H, 4.2; N, 5.0; S, 24.4; Cl, 13.4; Zn, 12.3. Found: C, 40.4; H, 3.9; N, 5.4; S, 24.1; Cl, 13.8; Zn, 11.9%.

(12) Diiodobis(ethyl N-phenyldithiocarbamate) diethanol - cadmium(II)

0.4 g (1 mmole) of CdI_2 in alcohol (8 ml) was added with stirring to a benzene solution (10 ml) of the ligand (1.0 g, ~ 5 mmole) and the resulting solution was refluxed for half an hour over a water-bath. A yellow oil was obtained by the addition of petroleum ether, which was separated, dissolved in chloroform and precipitated by petroleum ether. The process of recrystallization was repeated a few times until a pale yellow solid was obtained. It was dried under vacuum (m.p. 168-170°C) (yield, $\sim 65\%$).

Anal. Calcd for $[\text{CdI}_2(\text{EPD})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}]$: C, 31.0; H, 4.0; N, 3.3; S, 15.2; I, 29.8; Cd, 13.2. Found: C, 30.4; H, 3.8; N, 3.6; S, 14.9; I, 29.7; Cd, 12.8%.

(13) Dichlorobis(ethyl N-phenyldithiocarbamate)mercury(II)

HgCl_2 (0.27 g, 1 mmole) in alcohol (8 ml) was added to a solution of the ligand (1 g, ~5 mmole) in alcohol (10 ml) whereupon a white precipitate was immediately formed. Stirring was continued for an hour. The precipitate was centrifuged, washed with alcohol and ether. It was recrystallized from chloroform-petroleum ether and dried in vacuum (m.p. 220°C).

Anal. Calcd. for $[\text{HgCl}_2(\text{EPD})_2]$: C, 32.5; H, 3.3; N, 4.2; S, 19.3; Cl, 10.7; Hg, 30.1. Found: C, 31.9; H, 3.0; N, 4.4; S, 19.4; Cl, 11.0; Hg, 30.3%.

Analyses

(i) For the estimation of phosphorus, samples were decomposed by heating with Na_2O_2 , sugar and NaNO_3 in the ratio, 20:1:3 in a Parr-Bomb crucible and the melt was extracted with water. The extract was filtered and the filtrate was heated to sulphur trioxide fumes, after adding a few ml of concentrated H_2SO_4 . It was cautiously diluted with water and filtered, if necessary. In this solution, phosphorus was estimated as ammonium phosphomolybdate [2].

(ii) In order to estimate rhodium, samples were decomposed with a mixture of concn. H_2SO_4 and concn. HNO_3 . The solution

was evaporated to near dryness and the residue was extracted with water. From the extract, after filtration, rhodium was estimated as $[\text{Co}(\text{NH}_3)_6][\text{Rh}(\text{NO}_2)_6]$ [3].

(iii) Manganese, zinc, cadmium and mercury were estimated according to the standard methods as $\text{Mn}_2\text{P}_2\text{O}_7$, $[\text{Zn}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2]$, $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2]$ and HgS respectively, after decomposing the samples by a mixture of KNO_3 and KOH in a parrbomb crucible [4].

(iv) Nickel, palladium, copper, cobalt, iron, silver, sulphur, halide, carbon, hydrogen and nitrogen were estimated as described in Chapter II.

Infrared, magnetic susceptibility, conductivity and the electronic spectra of the ligand and complexes were taken by the usual procedure already described in Chapter II.

RESULTS AND DISCUSSION

The analytical data suggest that the ligand in all the complexes is functioning as monodentate, if one assumes that the metal ions take their normally preferred geometries [5a]. As a monodentate, it can link with metal ions through either nitrogen of the NH group or through thiocarbonyl or C-S sulphur atom. There is also a possibility of phenyl group entering into bonding with metal ions through its π -electrons and thus forming π -complexes [5b]. The i.r. spectral studies of the ligand and the complexes were taken to know the possible modes of linkages

in the complexes. In these studies, the tentative assignments of the bands were based on the comparative IR spectral studies of a number of related compounds given in the literature [6].

Infrared Spectra

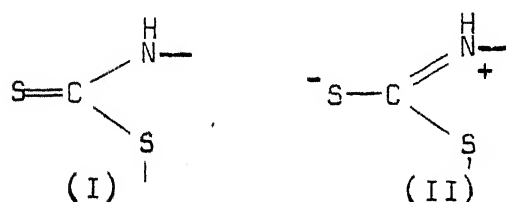
The infrared spectra ($4000\text{--}250\text{ cm}^{-1}$) of the ligand and its metal complexes are shown in Figs. III.1. The i.r. spectrum of the ligand showed characteristic bands due to phenyl and ethyl groups ($3130(b)$, 2980 , 2920 , 2880 , 1590 , 1500 , 1490 , 1440 , 1065 , 1008 , 750 , 690 cm^{-1}) [7a]. The positions of these bands remained practically constant ($\pm 5\text{ cm}^{-1}$) in the spectra of all the complexes. This suggests that the phenyl and ethyl groups are virtually unaffected by the complex formation. Although there is a possibility of forming π -type of complexes by the overlap of metal d-orbitals with phenyl π -orbitals, it is highly unlikely for phenyl group to participate in the bond formation when the more basic atoms like N and S are present in the ligand. It is, therefore, assumed that the metal ions in the complexes are bonded with -N(H)C(S)S- moiety of the ligand. Further, there is a definite possibility of the ligand to exist in the thiol form, -N=C(SH)-S- . This possibility is ruled out because of the absence of any band in the 2500 cm^{-1} region due to $\nu(\text{S-H})$ in its i.r. spectrum [7b]. The major shifts in the positions of the i.r. bands are, therefore, expected to be in those band positions, which are having contributions from (-NH) , (C=S) and (C-S) bonds. The changes in the band positions in the spectra

of the complexes, as compared to those of the ligand along with the discussion are as follows:

(a) A broad band at 3130 cm^{-1} along with a shoulder at 3200 cm^{-1} in the spectrum of the ligand, assigned to $\nu(\text{CH})$ of the phenyl group and $\nu(\text{NH})$ respectively, appeared as two separate bands around $3030\text{ cm}^{-1}(\text{w})$ and 3200 cm^{-1} in the spectra of the complexes. The broadness of the band in the ligand spectrum may be due to hydrogen bonding present in the solid state, which got considerably reduced in the complexes. This resulted in the separation of the band into discrete bands around 3030 cm^{-1} (due to $\nu(\text{CH})$ of the phenyl group) and around 3200 cm^{-1} (due to $\nu(\text{NH})$). The presence of the band due to $\nu(\text{NH})$ suggests that: (i) the NH group is not deprotonated and (ii) the nitrogen atom does not take part in the bond formation.

(b) Since the moiety, $-\text{N}(\text{H})\text{C}(=\text{S})\text{S}-$ contains a thioamide group ($\text{N}(\text{H})\text{CS}$), it should exhibit four characteristic bands due to thioamide group [7c]. The band at 1540 cm^{-1} in the spectrum of the ligand is assigned to the thioamide band (I), which arises due to the normal coordinate having major contributions from $\nu(\text{C}=\text{N})$ and $\delta(\text{NH})$. The position of this band was shifted towards higher wave numbers ($\sim 1550\text{ cm}^{-1}$) in the spectra of the complexes. If one assumes that the electronic structure of the ligand may be represented by a resonance hybrid of the structures I and II and coordination occurs through sulphur, the contribution of structure I will decrease after complexation. This may result in a decrease of the C=S bond order and thereby

shifting the position of $\nu(\text{C}=\text{S})$ towards lower wave numbers and that of $\nu(\text{C}=\text{N})$ towards higher wave numbers with no appreciable change in positions of NH modes of vibration [8a]:



Since thioamide band I contains major contribution from $\nu(\text{C}=\text{N})$ and $\delta(\text{NH})$, a shift in the position of this band towards higher wave number suggests the bonding through thiocarbonyl sulphur atom.

(c) The slightly broad band at 1330 cm^{-1} in the spectrum of the ligand has been assigned to thioamide band (II), which has major contribution from $\nu(\text{C}=\text{N})$ and $\delta(\text{NH})$. In the spectra of all the complexes, the position of this band shifted towards higher wave numbers ($\sim +30\text{ cm}^{-1}$). This shift could be easily explained if the bonding of the metal ions occurs through thiocarbonyl sulphur as assumed in (b) above.

(d) The position of the thioamide band (III) which appears at 1050 cm^{-1} in the spectrum of ligand has been shifted towards lower wave numbers ($\sim -15\text{ cm}^{-1}$) in the spectra of all the complexes. Since this band arises due to normal coordinate having major contribution from $\nu(\text{C}=\text{N})$ and relatively less from $\nu(\text{C}=\text{S})$, one should expect a little shift in the position of this band [because of the contribution from $\nu(\text{C}=\text{S})$] in the

spectra of the complexes, if the bonding occurs as discussed in (b) above.

(e) Thioamide band (IV) which contains a major contribution from $\nu(\text{C}=\text{S})$ appeared at 970 cm^{-1} in the spectrum of the ligand. The position of this band was shifted to around 920 cm^{-1} in the spectra of the complexes [9]. This observation is quite in conformity with what one should expect, if the bonding of the metal ions is assumed to be through thiocarbonyl sulphur atom because of the reduction in the bond order of $(\text{C}=\text{S})$ in complexes after bonding.

(f) The position of the band at 730 cm^{-1} in the spectra of the ligand, assigned to $\nu(\text{C}-\text{SEt})$ is slightly shifted to higher wave numbers ($\sim +5\text{ cm}^{-1}$) in conformity with the assumption of $\text{M}-\text{S}=\text{C}<$ bonding.

(g) In the spectra of the complexes having PPh_3 or AsPh_3 as coligands, all the characteristic bands due to PPh_3 or AsPh_3 have been exhibited by the spectra of the complexes [10].

(h) There appeared one (broad) or two (relatively less broad) new bands around 300 cm^{-1} in the spectra of the complexes. These have been assigned to the coupled vibrations of $\nu(\text{M}-\text{S})$ with other bending modes of the ligand molecule [11]. A new band appeared in the complex of Ru(II) at 280 cm^{-1} . It may be due to $\text{Ru}-\text{Cl}-\text{Ru}$ bridge [11].

(i) The characteristic bands of NO_3^- in the silver complex were present in its spectrum, suggesting the presence of NO_3^- group [8b].

Thus, it has been assumed, on the basis of i.r. studies that the metal ions in the complexes are linked with thio-carbonyl sulphur atom and possibly acting as monodentate towards a metal ion.

Magnetic Moment

All the complexes, except those of iron(II) and cobalt(II), exhibited diamagnetic behaviour. $\text{CoCl}_2(\text{EPD})_2 \cdot \text{EtOH}$ is paramagnetic with an observed moment of 2.05 B.M. On the basis of magnetic moment, it is difficult to distinguish between spin paired octahedral and square planar complexes of cobalt(II) as, in principle, for both the cases the moment should be close to spin only value for one unpaired electron. In practice, there are very few known low spin octahedral complexes of Co(II) and such complexes especially with sulphur ligands of low crystal field strength which possess the magnetic moments lying in the range, 1.8-2.0 BM [12] are rather unknown. However, the values of several Co(II) complexes having definite square planar configuration fall in the range of 2.1 - 2.8 B.M. [12,13]. On the basis of the above argument, it is suggested that the complex, $[\text{CoCl}_2(\text{EPD})_2] \cdot \text{EtOH}$ has the low spin square planar geometry (d^7 system) and cobalt exists in +2 oxidation state.

The magnetic moment of iron(II) complex was found to be 5.2 B.M. corresponding to four unpaired electrons. The ground state of Fe(II) in high spin octahedral complexes [14] is

$^5T_{2g}$ and that in complexes having T_d symmetry is 5E . Whatever may be the geometry of the Fe(II) complex (octahedral or tetrahedral), the number of unpaired electrons on the iron ion will be four and there will be a certain amount of orbital contribution to the spin only value of the magnetic moment. In practice, the value of the magnetic moment of tetrahedral Fe(II) complex is found to be around 5.2 B.M. and that of octahedral complex, around 5.4 B.M.[15]. The value of magnetic moment of 5.2 B.M. for the complex under discussion suggested the tetrahedral geometry of the Fe(II) complex. This geometry is also consistent with the composition of the complex, $[FeCl_2(EPD)_2]$ in which every ligand is acting as monodentate. Although four coordinated complex can have only two possible geometries (tetrahedral or square planar), square planar geometry is however ruled out because of the fact that the value of the magnetic moment for such complexes will be corresponding to two unpaired electrons (> 2.8 B.M.). Tetrahedral geometry is, therefore, assigned to the iron complex.

The diamagnetism of Ru(II) complex is not surprising. Since all the known octahedral complexes of ruthenium(II) have been found to be diamagnetic [5c]. It is assumed that the ruthenium complex possesses the octahedral geometry around the metal ion.

There is hardly any complex known of Rh(I) and Rh(III) which is paramagnetic and have geometries other than square

planar and octahedral, respectively [5d]. Therefore, the complexes, $[\text{RhCl}(\text{EPD})_2(\text{PPh}_3)]$ and $[\text{RhCl}_3(\text{EPD})_3]$ have been assigned square planar and octahedral geometries, respectively which are the preferred ones for Rh(I) and Rh(III) ions in their complexes.

$[\text{NiCl}_2(\text{EPD})_2]$ and $[\text{PtCl}_2(\text{EPD})_2]$ are diamagnetic. The diamagnetic behaviour of these complexes reveals the square-planar geometry around Ni(II) and Pt(II) complexes [15b]. It is well known that all the diamagnetic four coordinated complexes of Pt(II) and Ni(II) have square planar geometry. However, the four coordinated Ni(II) complexes may also take up tetrahedral geometry and the latter is ruled out because of the fact, the tetrahedral nickel complexes must show paramagnetism corresponding to two unpaired electrons. It is, therefore, presumed that the diamagnetic four coordinated Ni(II) complex has square-planar geometry.

$\text{Pd}(0)$, $\text{Pt}(0)$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ complexes are found to be diamagnetic and belong to d^{10} system. The only possible geometry which the four coordinated complexes of these metal ions could take is tetrahedral which should exhibit diamagnetic behaviour [5e]. Therefore, these complexes have been assigned tetrahedral geometry.

Silver complex is diamagnetic and has coordination number two, when the nitrate ion has been assumed to have ionic bonding. It has, therefore, been assumed that the silver complex has the linear geometry [5f].

Electronic Spectra

The electronic spectrum of the ligand showed three relatively weak bands at 300 nm, 285 nm and 235 nm. The position of the bands at 300 nm and 285 nm were shifted towards lower wave length region in the spectra of the complexes which may be explained as follows. In case the metal ions are bonded to thiocarbonyl sulphur atom, the lone pair of electrons on the thiocarbonyl sulphur acts as an electron donor to the metal centre of the complex to form M-S bond. The formation of this bond lowers the energy of the non-bonding orbitals of the thiocarbonyl sulphur atom [16a]. Now in the $n \rightarrow \pi^*$ transition which is responsible for the appearance of the band at 300 nm and 285 nm, one of the electrons is removed from the non-bonding orbital and promoted to π^* orbital whose energy (π^* orbital) remains unaffected. Therefore, the hypsochromic shift of this band on complexation indicates that it is due to $n \rightarrow \pi^*$ transition and the bonding of metal ion takes place through thiocarbonyl sulphur.

The position of band at 235 nm remained unaffected on complexation, suggesting it to arise from a transition between two energy levels which remained unaffected by metal complexation. It is suggested that the band arises due to $\pi \rightarrow \pi^*$ transition of the phenyl ring [16b].

The electronic spectrum of cobalt complex, $\text{CoCl}_2(\text{EPD})_2 \cdot \text{C}_2\text{H}_5\text{OH}$ showed a very weak band in the near infrared region at

1800 nm, which is characteristic of a square planar Co(II) species [17-20]. This result is corroborated by its magnetic data (2.02 B.M.). The intense bands at 730 nm, 650 nm and 620 nm may be charge transfer bands.

The spectrum of nickel complex showed a relatively weak band at 560 nm with a shoulder at 500 nm. This low intensity band is ascribed to d-d transition in square planar complexes and assigned as $^1A_g \rightarrow ^1B_{1g}$, based on D_{2h} micro-symmetry [21]. The absence of the bands around 2000 nm, 1000 nm and 400 nm rules out the tetrahedral or octahedral geometry of the complex. This is consistent with the diamagnetic behaviour of the complex.

The ground state of ruthenium(II) and rhodium(III) in the octahedral complexes is $^1A_{1g}$ and the excited states are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$, $^1T_{2g}$. One should, therefore, expect four bands due to transitions from $^1A_{1g}$ to $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in the spectra of octahedral complexes of these metal ions [14]. In general, singlet \rightarrow triplet transitions are very weak and are not usually observed. Further, the spectrum of the Ru(II) complexes showed charge transfer bands upto 550 nm and most of the weak d-d bands were, therefore, masked by them. However, one weak and broad band at 620 nm was exhibited in the spectrum of the Ru(II) complex which could possibly be assigned to either $^1A_{1g} \rightarrow ^1T_{1g}$ or $^1A_{1g} \rightarrow ^1T_{2g}$, analogous to other Ru(II) complexes [22-24]. In the spectrum of Rh(III) a weak band appeared at 470 nm which is assigned to either $^1A_{1g} \rightarrow ^1T_{1g}$ or $^1T_{2g}$ transition. The shift

of the position of band in Rh(III) complex towards high energy region may be due to the increased charge on rhodium as compared to ruthenium with the resulting increase in $10 Dq$ value [15c].

In the spectra of Rh(I), Pd(0), Pt(0), Ag(I), Zn(II), Cd(II) and Hg(II), the bands did not appear in the visible region. In the case of Rh(I), the intense charge transfer band moved in the visible region, thereby masking all the weak d-d transition bands. In the rest of the complexes, the electronic configuration of the metal ions is d^{10} and one should, therefore, not expect any band in the visible or in the near i.r. region.

Iron(II) and platinum(II) complexes did not show any band in the visible region because of the presence of intense charge transfer bands. In consonance with the fact that all the known complexes of Pt(II) were found to be square planar, the present Pt(II) complex has been assigned the same geometry. It is also supported by its diamagnetic behaviour.

On the basis of the analytical, spectral (ir, uv, visible) and magnetic moment data, it is inferred that the bonding of metal ion takes place through thiocarbonyl sulphur and the ligand is acting as monodentate. The following geometries have been tentatively assigned to the complexes:

- (i) $[RuCl_2(EPD)_3]$ - Octahedral with possibly Ru-Cl-Ru bridge
- (ii) $[RhCl_3(EPD)_3]$ - Octahedral

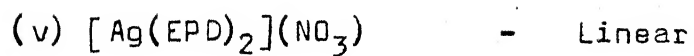
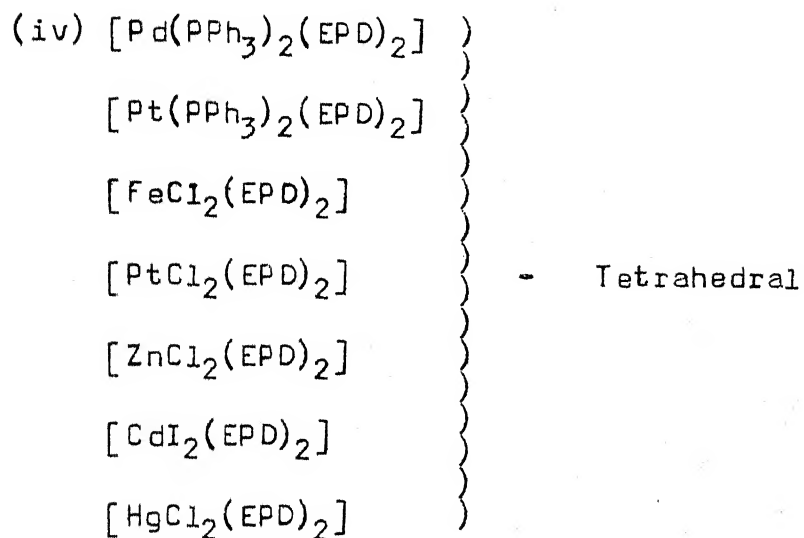
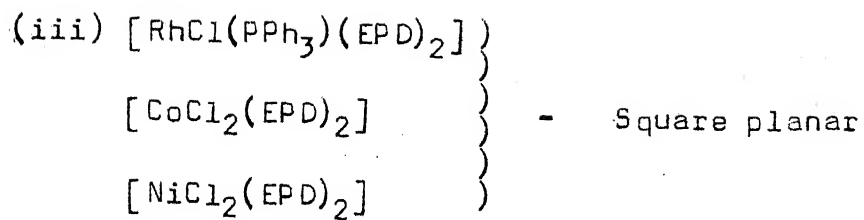


Table III.1

Assignments of Major IR Bands of the Ligand
and its Complexes

EPD (cm^{-1})	Complexes (cm^{-1})	Assignments
3130(m)	3030(m)	$\nu(\text{CH})$ of the phenyl group
3200(sh)	3200(m)	$\nu(\text{NH})$
1540(m)	1550(m)	Thioamide band I, contributions from $\nu(\text{C}=\text{N}) + \delta(\text{NH})$
1330(s)	$\sim 1360(\text{m})$	Thioamide band II, contributions from $\nu(\text{C}=\text{N})$ and $\delta(\text{NH})$
1050(s)	$\sim 1035(\text{m})$	Thioamide band III, contributions from $\nu(\text{C}-\text{N}) + \nu(\text{C}=\text{S})$
970(m)	920(w)	Thioamide band IV, contribution mainly from $\nu(\text{C}=\text{S})$
730(m)	$\sim 735(\text{m})$	$\nu(\text{C}-\text{S Et})$
-	300(m)	One or two bands due to $\nu(\text{M}-\text{S})$ coupled with other bending modes of the ligand
-	280(m) (in Ru(II) complex)	Ru-Cl-Ru bridge

(m), medium; (sh), shoulder; (s), strong; (w), weak.

Table III.2

Mag. Moments, Absorption Bands in the Electronic Spectra of the Ligand
and its Complexes with Their Assignments

Compound	Magnetic Moment (B.M.)	Absorption band nm (cm^{-1})	Assignments
EPD	-	235 (42,553)	$\pi \rightarrow \pi^*$ of the phenyl ring
$[\text{CoCl}_2(\text{EPD})_2 \cdot \text{C}_2\text{H}_5\text{OH}]$	2.02	1800(w) (5,556)	Square planar Co(II) species
		730 (13,699) } 650 (15,385) } 620 (16,129) }	Charge transfer bands
$[\text{NiCl}_2(\text{EPD})_2]$	DM	560(w) (17,857) 500(sh) (20,000)	$^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$
$[\text{RuCl}_2(\text{EPD})_3]$	DM	620 (16,129)	$^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ or $^1\text{T}_{2g}$
		550 (18,182)	Charge transfer band
$[\text{RhCl}_3(\text{EPD})_3]$	DM	470(w) (21,277)	$^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ or $^1\text{T}_{2g}$

DM, diamagnetic; (w), weak; (sh), shoulder.

LEGEND TO THE FIGURES

Fig. III.1 Infrared Spectra of EPD and its Complexes:

- (1) EPD
- (2) $[\text{FeCl}_2(\text{EPD})_2]$
- (3) $[\text{RuCl}_2(\text{EPD})_3]$
- (4) $[\text{CoCl}_2(\text{EPD})_2] \cdot \text{C}_2\text{H}_5\text{OH}$
- (5) $[\text{RhCl}_3(\text{EPD})_3]$
- (6) $[\text{RhCl}(\text{PPh}_3)(\text{EPD})_2]$
- (7) $[\text{NiCl}_2(\text{EPD})_2]$
- (8) $[\text{Pd}(\text{PPh}_3)_2(\text{EPD})_2]$
- (9) $[\text{Pt}(\text{PPh}_3)_2(\text{EPD})_2]$
- (10) $[\text{PtCl}_2(\text{EPD})_2]$
- (11) $[\text{Ag}(\text{EPD})_2](\text{NO}_3)$
- (12) $[\text{ZnCl}_2(\text{EPD})_2]$
- (13) $[\text{CdI}_2(\text{EPD})_2] \cdot 2\text{C}_2\text{H}_5\text{OH}$
- (14) $[\text{HgCl}_2(\text{EPD})_2]$

Fig. III.2 Electronic Spectra of EPD and its Complexes:

- (1) EPD
- (2) $[\text{FeCl}_2(\text{EPD})_2]$
- (3) $[\text{RuCl}_2(\text{EPD})_3]$
- (4) $[\text{CoCl}_2(\text{EPD})_2] \cdot \text{C}_2\text{H}_5\text{OH}$
- (5) $[\text{RhCl}_3(\text{EPD})_3]$
- (6) $[\text{RhCl}(\text{PPh}_3)(\text{EPD})_2]$
- (7) $[\text{NiCl}_2(\text{EPD})_2]$

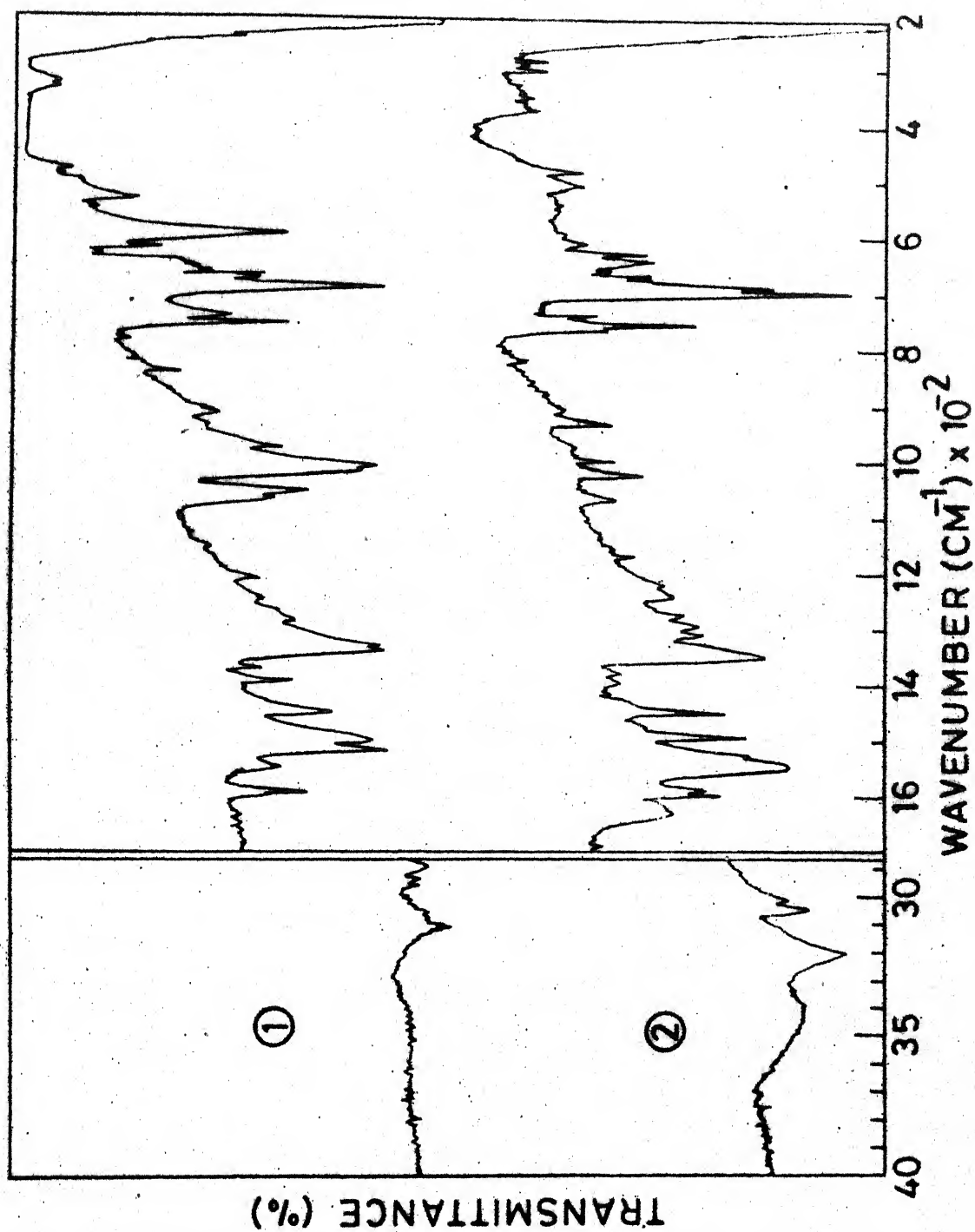


FIG. III. 1 INFRARED SPECTRA OF ① & ② .

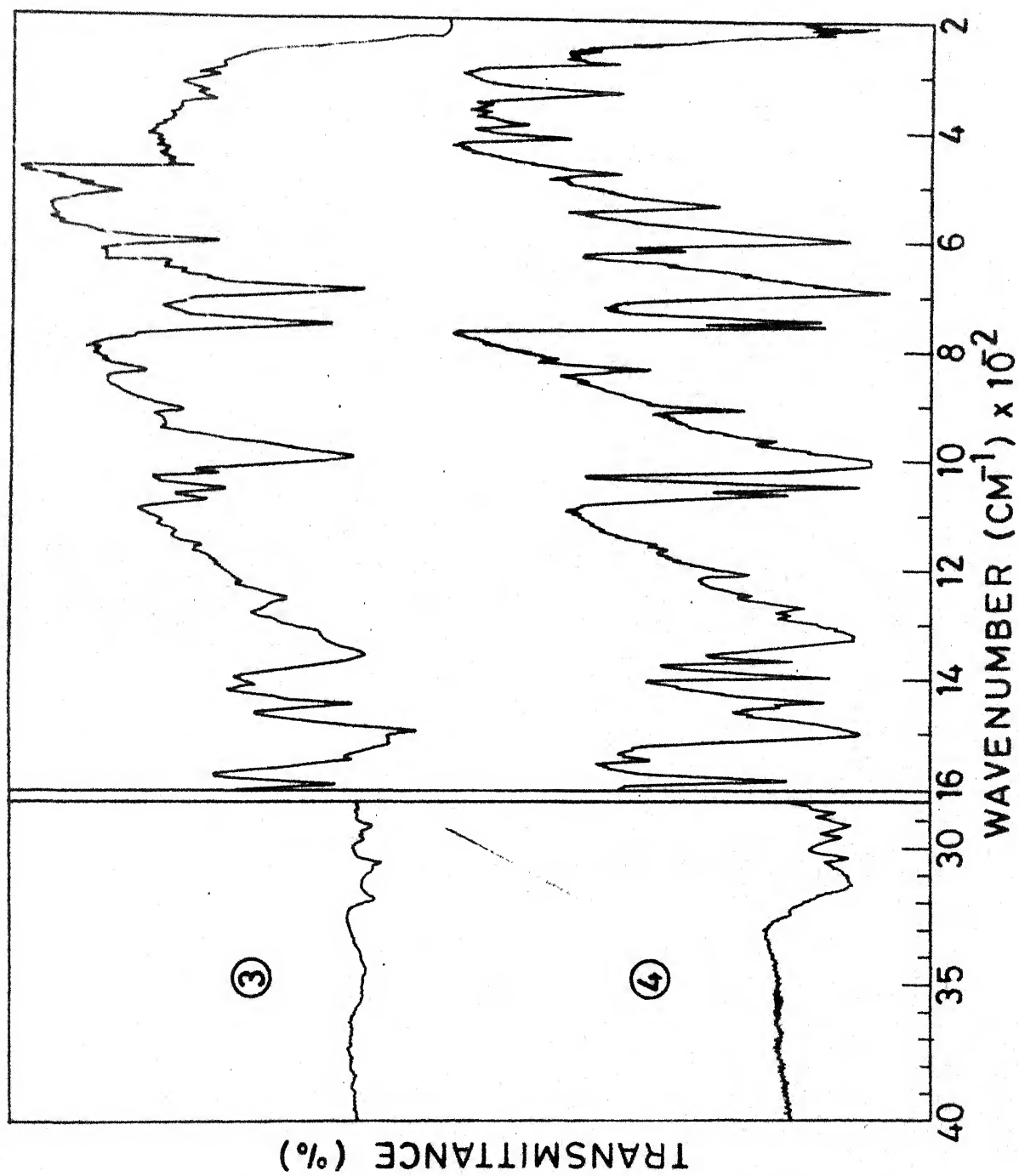


FIG. III .1 INFRARED SPECTRA OF ③ & ④

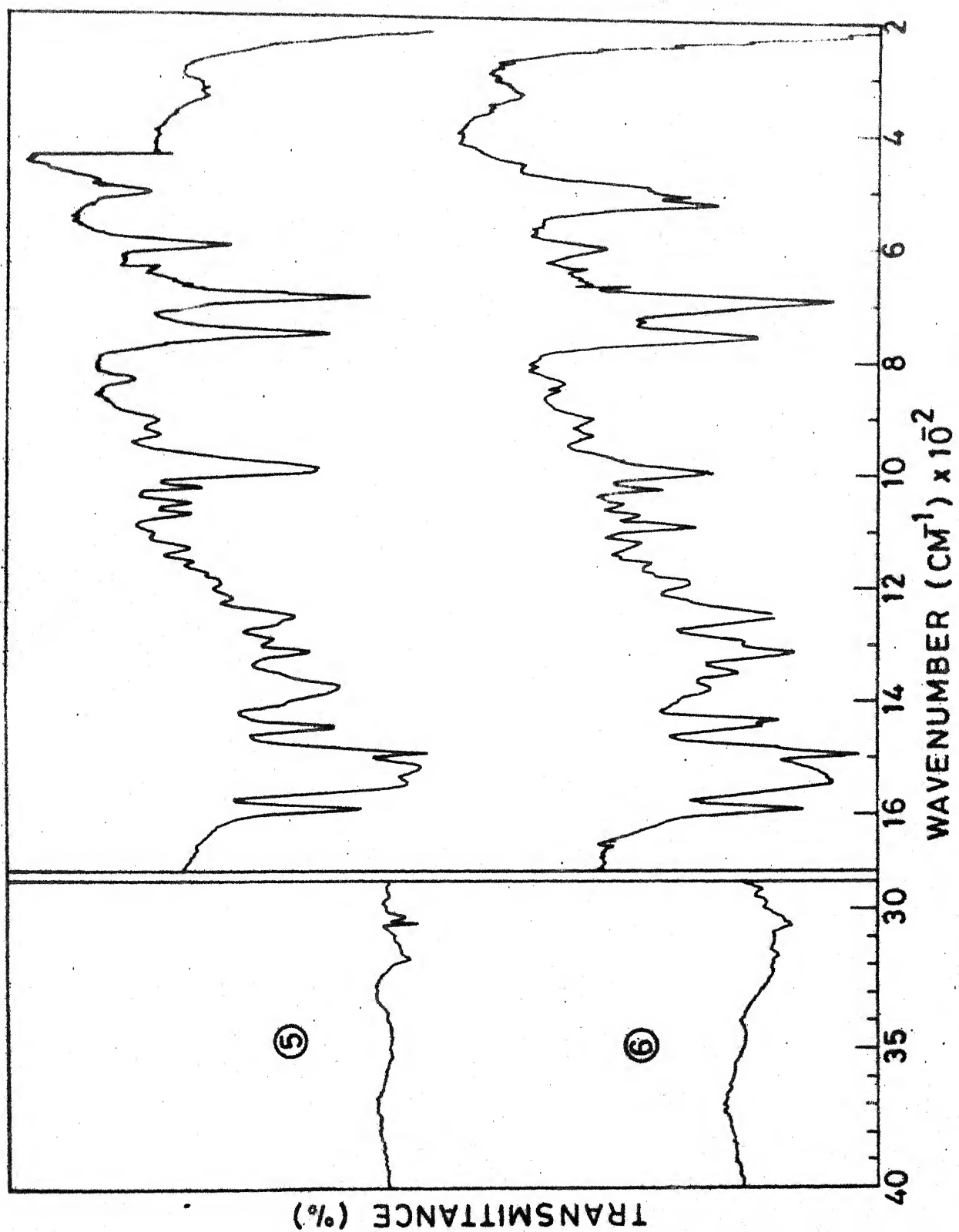


FIG. III.1 INFRARED SPECTRA OF ⑤ & ⑥ .

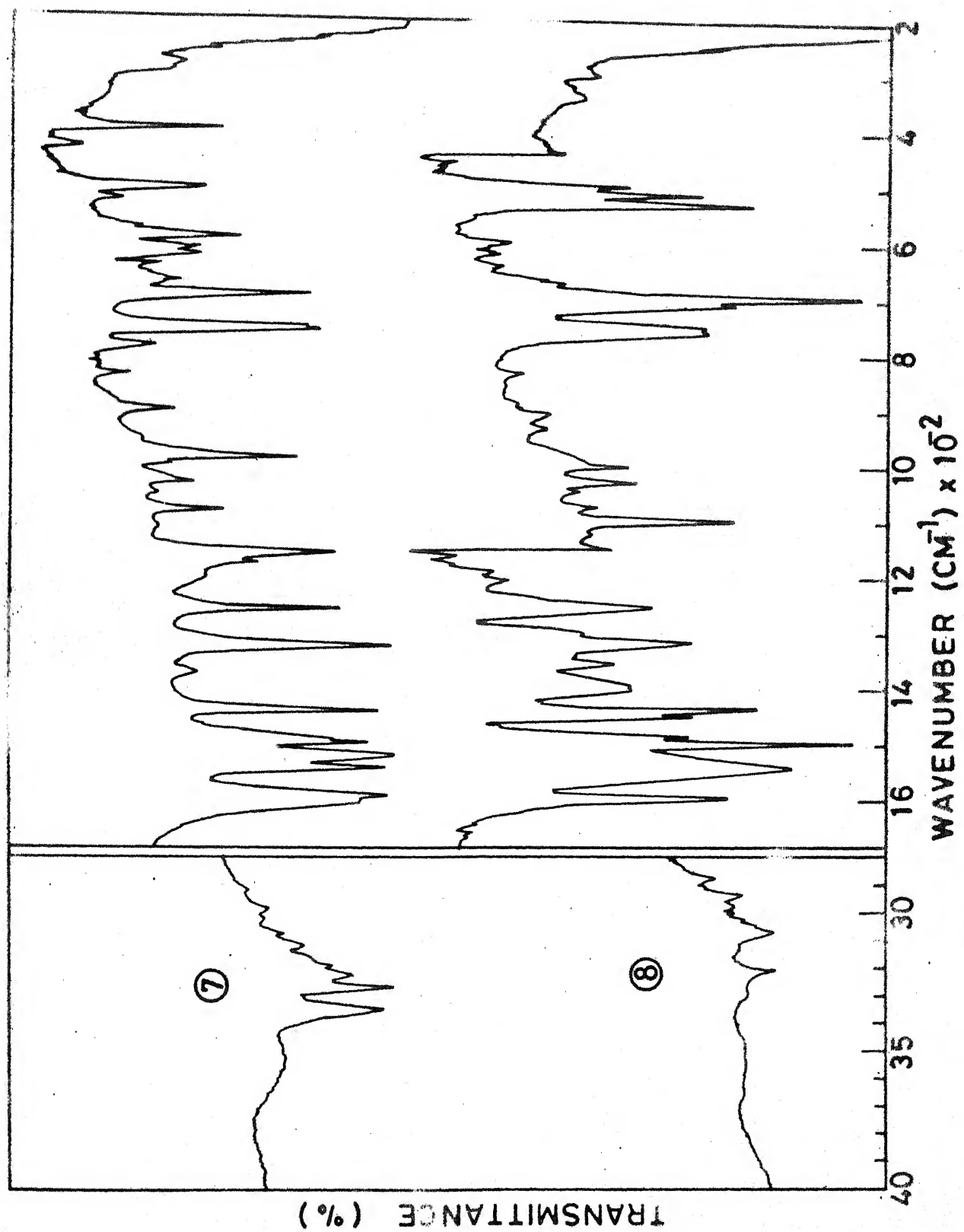


FIG. III.1 INFRARED SPECTRA OF ⑦ & ⑧.

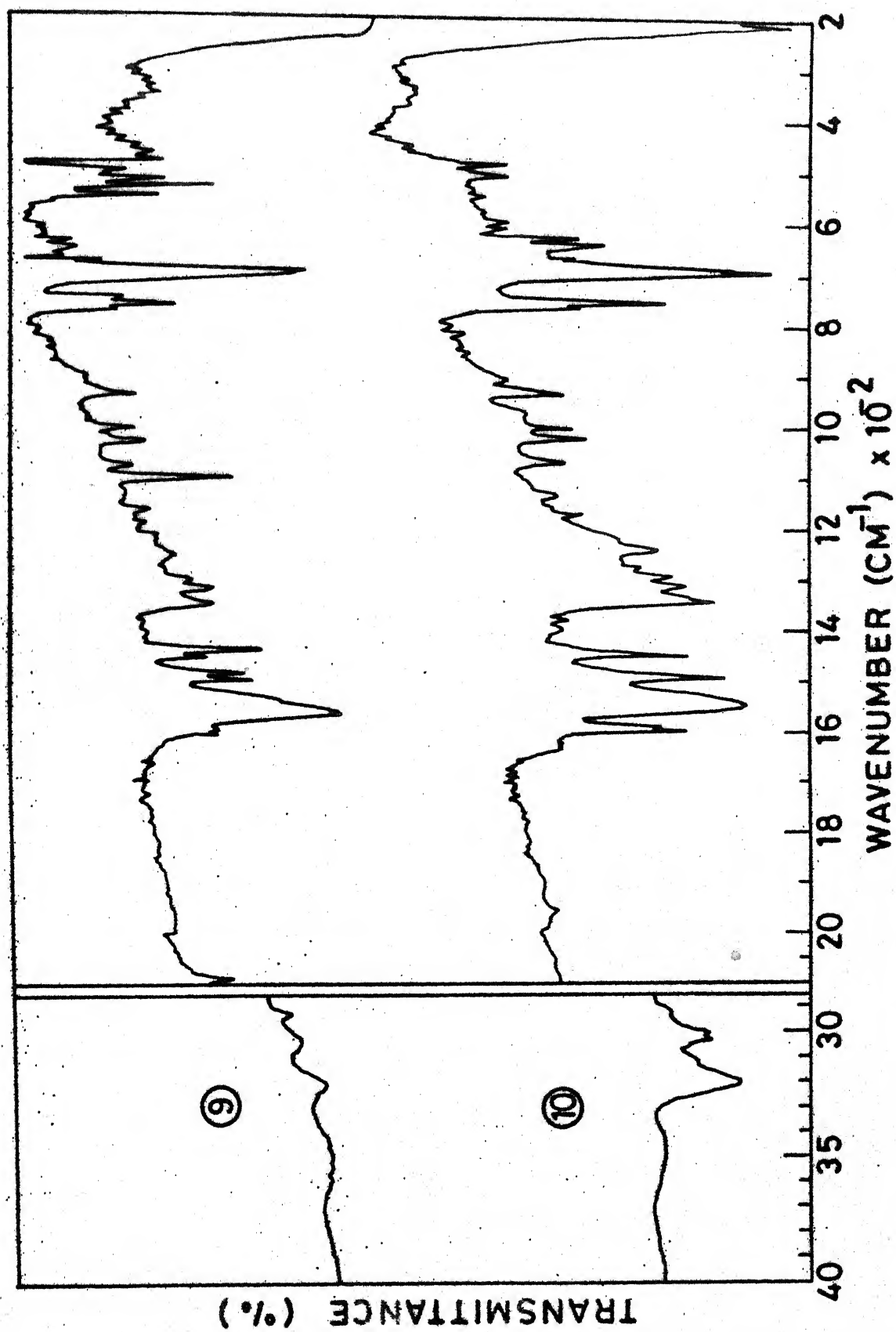


FIG. III.1 INFRARED SPECTRA OF ⑨ & ⑩ .

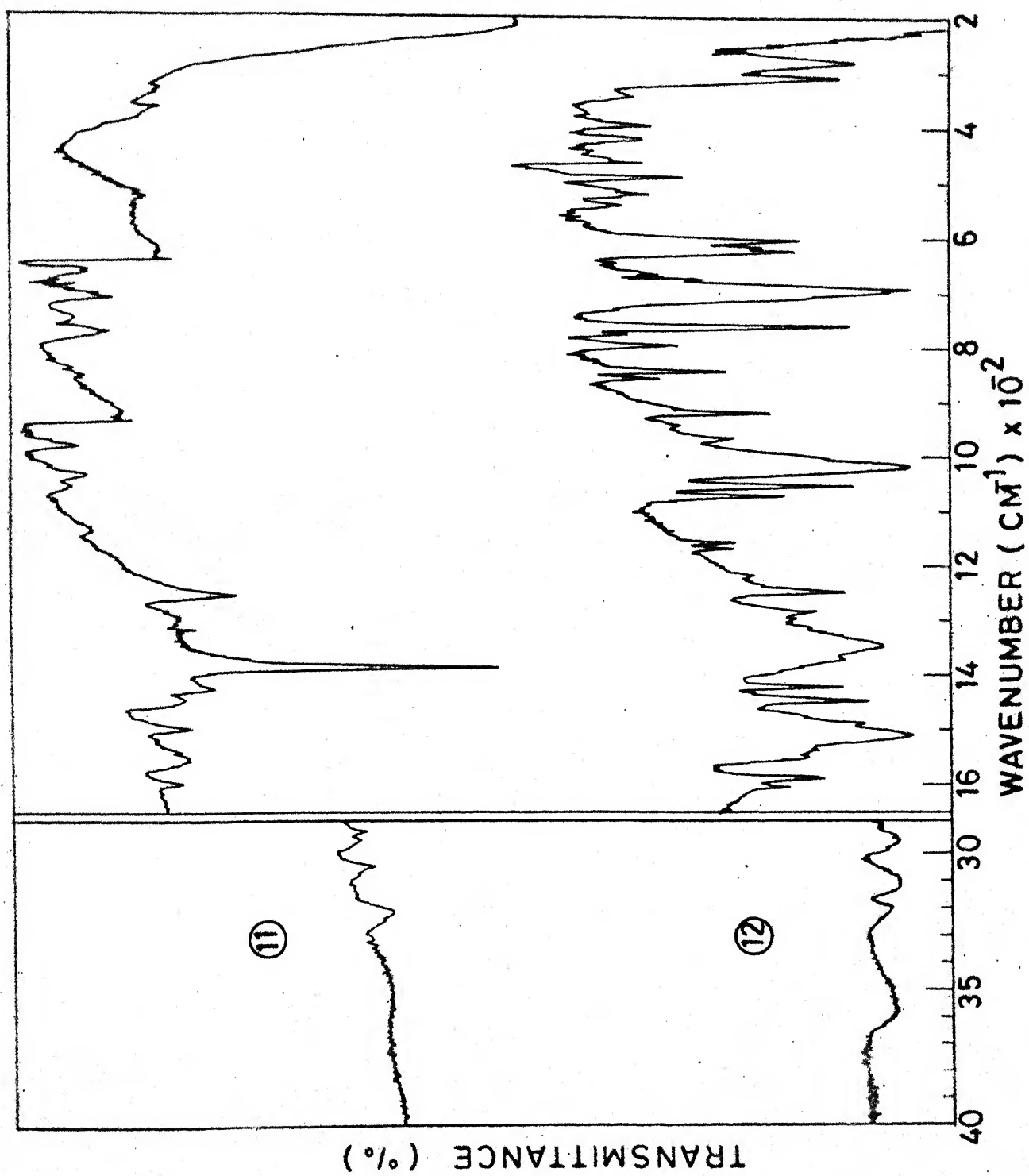


FIG. III.1 INFRARED SPECTRA OF ⑪ & ⑫

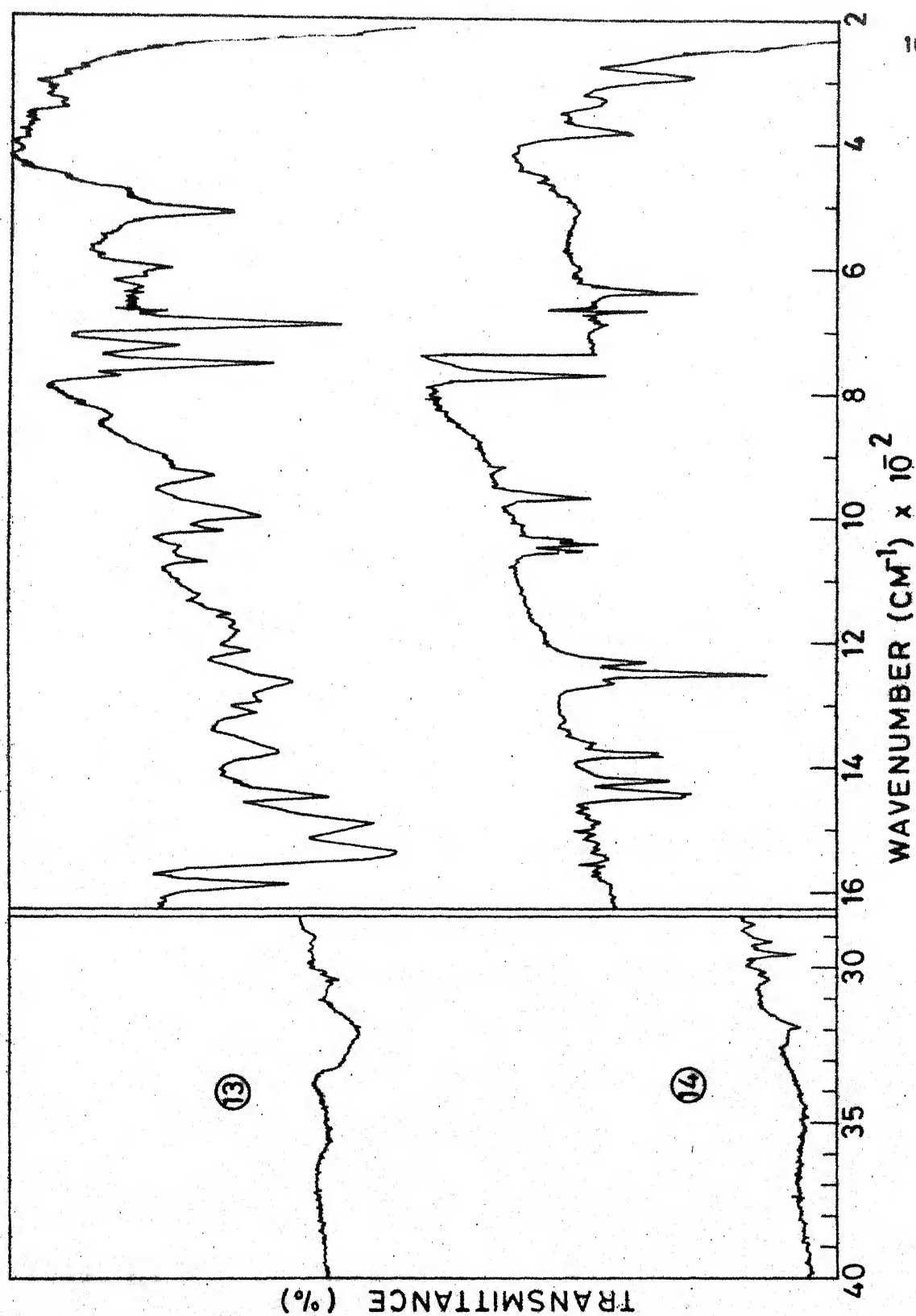


FIG. III.1 INFRARED SPECTRA OF 13 & 14

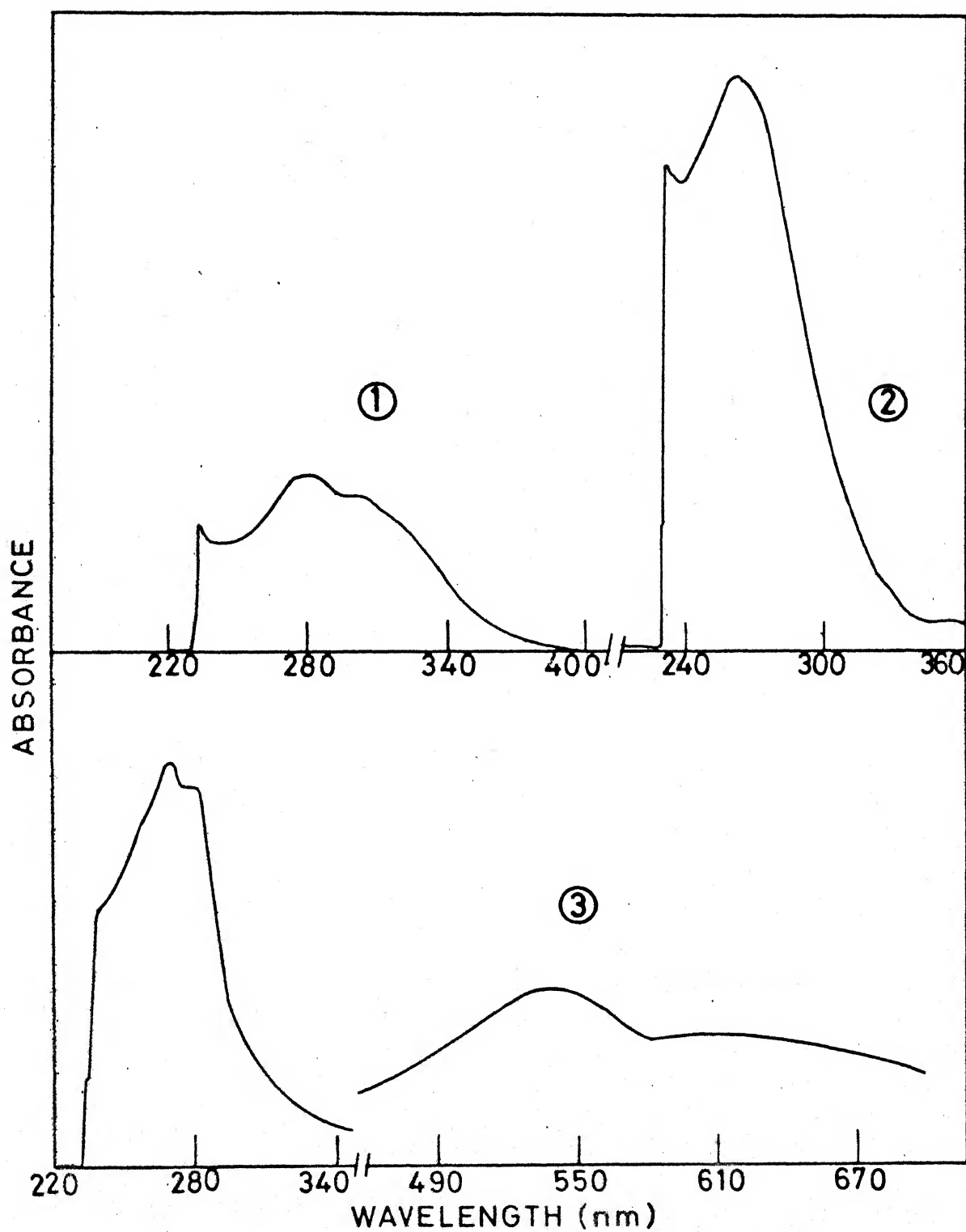


FIG. III.2 ELECTRONIC SPECTRA OF ①, ② & ③.

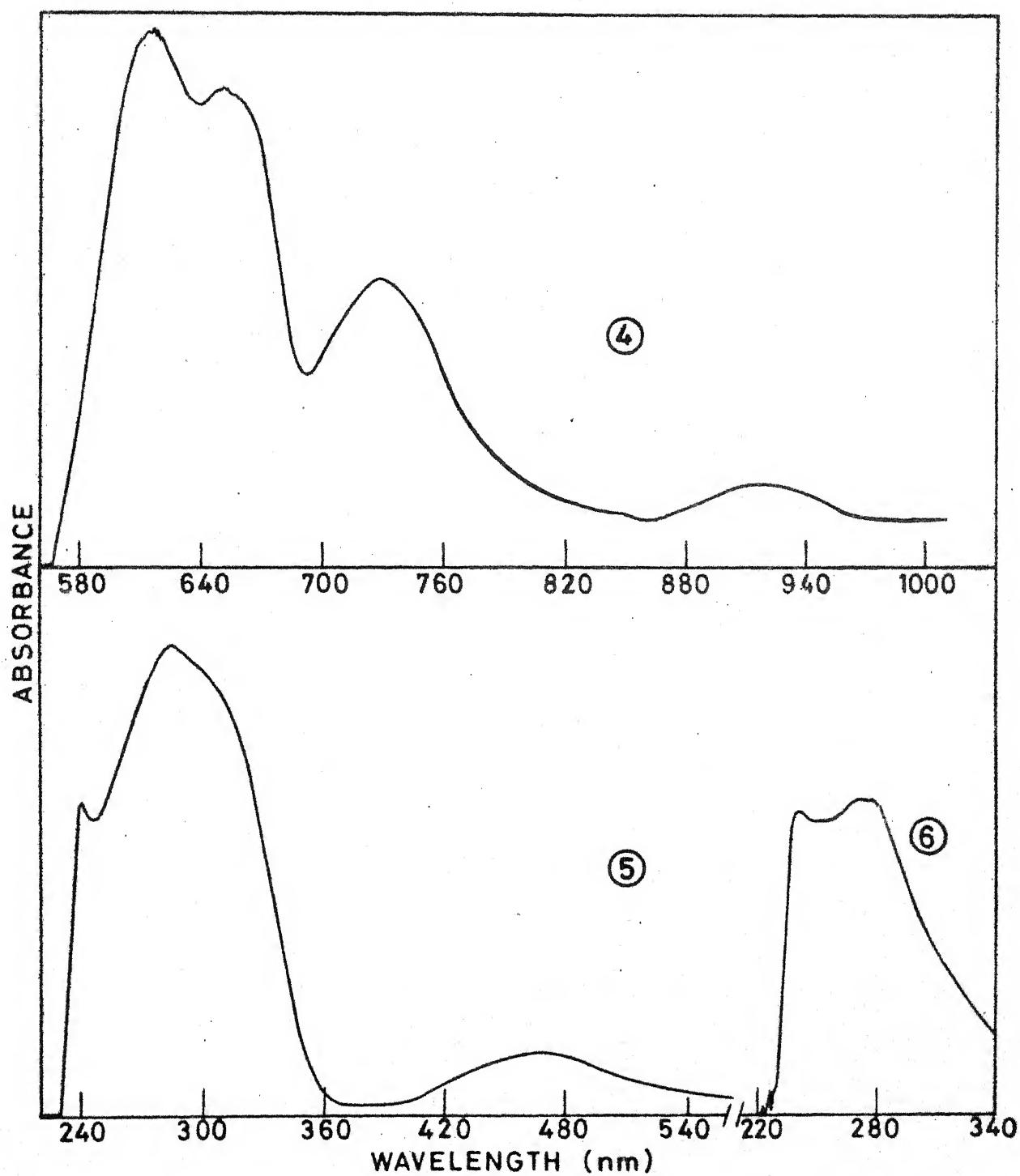


FIG. III.2 ELECTRONIC SPECTRA OF ④ , ⑤ & ⑥

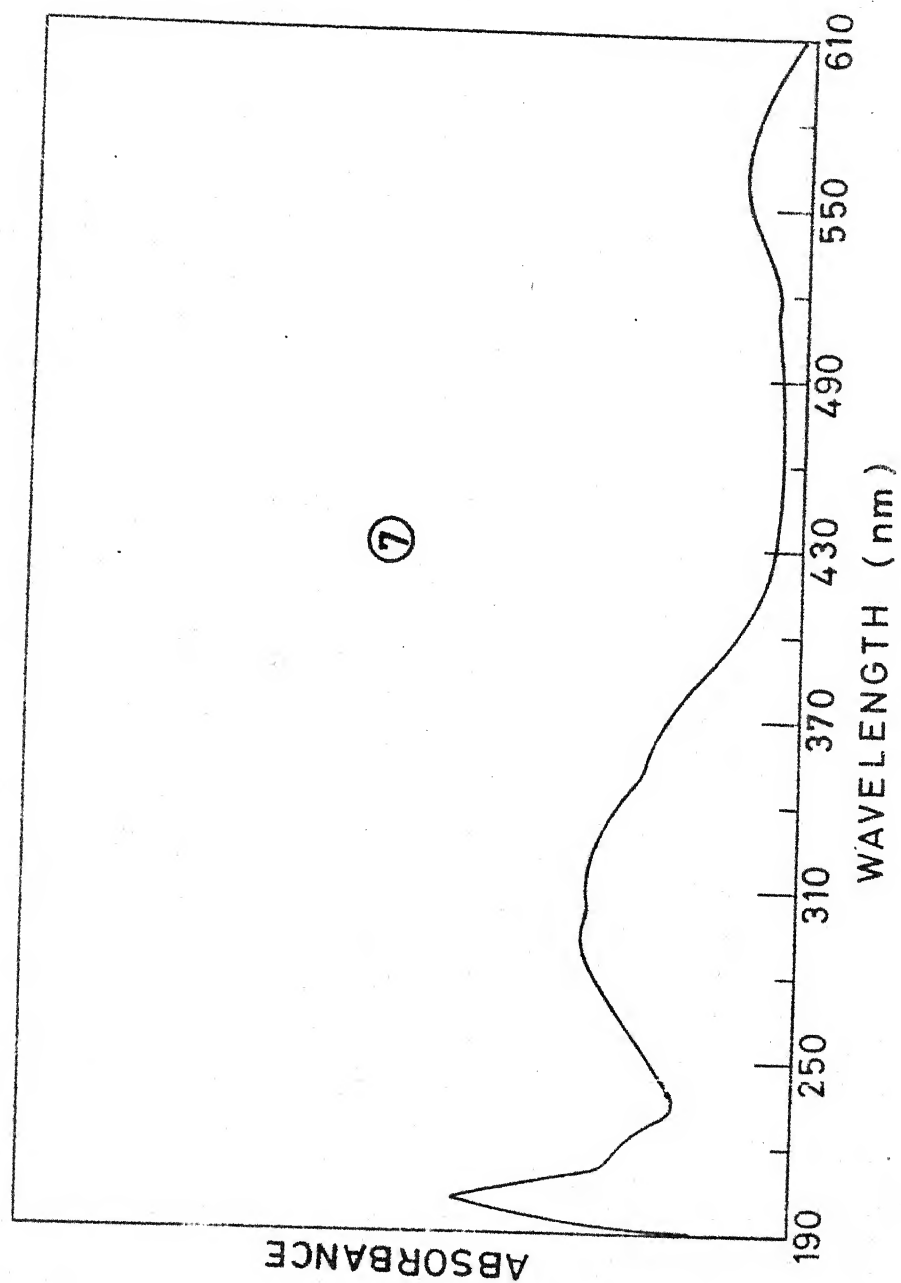


FIG. III.2 ELECTRONIC SPECTRUM OF ⑦

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CHAPTER IV

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COMPLEXING BEHAVIOUR OF N-SULPHINYLANILINE: COMPLEXES OF Mn(II), Fe(II), Ru(II), Co(I), Rh(I), Ni(O), Pd(O), Pt(O), Cu(I) and Ag(I)

This chapter deals with the preparations, the magnetic and the spectroscopic (i.r., u.v. and visible) studies of the complexes of Mn(II), Fe(II), Ru(II), Co(I), Rh(I), Ni(O), Pd(O), Pt(O), Cu(I) and Ag(I) with N-sulphinylaniline (NSA). The probable structures of the resulting complexes have been postulated on the basis of analytical, spectral and magnetic data.

EXPERIMENTAL

All the chemicals used were chemically pure or of Analar grade. All the solvents were distilled and dried by standard procedures prior to use.

N-Sulphinylaniline, Dichlorobis(triphenylphosphine)iron(II), Dichlorotris(triphenylphosphine)ruthenium(II), Trichlorobis(triphenylarsine)methanol ruthenium(III), Hydridotetrakis(triphenylphosphite)cobalt(I), Chlorotris(triphenylphosphine)rhodium(I), Carbonylchlorobis(triphenylphosphine)rhodium(I), Tetrakis(triphenylphosphite)nickel(0), Tetrakis(triphenylphosphine)palladium(0), Tetrakis(triphenylphosphine)platinum(0), Chlorotris(triphenylphosphine)copper(I) and Tetrakis(triphenylphosphine)silver(I) nitrate have been prepared by reported methods [1-11].

Preparation of Complexes

(1) Dichlorobis(N-sulphinylaniline)manganese(II)

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.8 g, ~4 mmole) was dissolved in 10 ml of ethyl alcohol and kept mechanically stirred. The solution of the ligand, (NSA) (2.5 ml, ~16 mmole) in 10 ml of alcohol was slowly added to it and stirring was further continued for an hour, whereupon a pale pink complex got separated which was centrifuged, washed for a few times with alcohol and finally with ether. The vacuum dried sample was found to be not melting upto 300°C (yield, ~55%).

Anal. Calcd. for $[\text{MnCl}_2(\text{NSA})_2]$: C, 35.6; H, 2.5; N, 6.9; S, 15.8; Cl, 17.8; Mn, 13.6. Found: C, 35.3; H, 2.4; N, 6.7; S, 16.1; Cl, 18.1; Mn, 13.4%.

(2) Dichloro(triphenylphosphine)(N-sulphinylaniline)iron(II)

Dichlorobis(triphenylphosphine)iron(II) (1.2 g, ~2 mmole) was dissolved in 15 ml of benzene by warming over a water bath. To the resulting clear solution, 10 ml of the benzene solution of the ligand, NSA (1.6 ml, ~10 mmole) was added and refluxed over a water-bath for about an hour. The resulting dark brown solution was concentrated to half of its original volume. On addition of 15 ml petroleum ether (40-60°) to it, yielded a greyish-green complex which was centrifuged and washed with petroleum ether. It was recrystallized twice from benzene-petroleum ether and dried in a vacuum desiccator (m.p. 185-186°C) (yield, ~60%).

Anal. Calcd. for $[\text{FeCl}_2(\text{PPh}_3)(\text{NSA})]$: C, 54.6; H, 3.8; N, 2.7; S, 6.1; Cl, 13.5; Fe, 10.6. Found: C, 54.2; H, 3.6; N, 2.4; S, 6.2; Cl, 13.8; Fe, 10.3%.

(3) Dichlorobis(triphenylphosphine)bis(N-sulphinylaniline)-ruthenium(II)

The ligand, NSA (0.5 ml, ~3 mmole) in 6-7 ml of chloroform was very slowly added to a dark brown solution of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.5 g, ~0.5 mmole) in 10 ml of chloroform, under well-stirred conditions. A blue complex was immediately

precipitated and stirring was continued for about an hour more. The blue complex was separated by filtration and washed with petroleum ether. It was recrystallized by dissolving it in the minimum amount of chloroform, followed by the addition of petroleum ether. The process of recrystallization was repeated several times, until a constant melting complex was finally obtained (m.p. 190-192°C)(yield, ~65%).

Anal. Calcd. for $[\text{RuCl}_2(\text{PPh}_3)_2(\text{NSA})_2]$: C, 59.1; H, 4.1; N, 2.9; S, 6.6; Cl, 7.3. Found: C, 58.8; H, 3.7; N, 3.2; S, 6.5; Cl, 7.6%.

(4) Dichlorobis(triphenylarsine)bis(N-sulphinylaniline)-ruthenium(II)

$\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{MeOH}$ (0.43 g, ~0.5 mmole) was dissolved in dichloromethane (10 ml) and a solution of the ligand, NSA (0.5 ml, ~3 mmole) in 10 ml of benzene was mixed gradually. The resulting brown solution was stirred for about two hours and its volume was reduced to about 10 ml over a water-bath. 10 ml of petroleum ether (40-60°C) was added to the resulting dark brown solution, whereby a brown complex was precipitated. It was filtered, washed with n-pentane and recrystallized from dichloromethane-petroleum ether (m.p. 176-177°C)(yield, ~60%).

Anal. Calcd. for $[\text{RuCl}_2(\text{AsPh}_3)_2(\text{NSA})_2]$: C, 54.2; H, 3.8; N, 2.6; S, 6.0; Cl, 6.7. Found: C, 54.4; H, 3.4; N, 2.4; S, 5.6; Cl, 7.0%.

(5) Hydridobis(triphenylphosphite)(N-sulphinylaniline)cobalt(I)

Hydridotetrakis(triphenylphosphite)cobalt(I) (1.4 g , ~1 mmole) was dissolved in 15 ml of acetonitrile and a benzene solution (10 ml) of the ligand, NSA (1 ml, ~6 mmole) was added under stirring condition. During the course of stirring for 1.5 hrs, the colour of the pale yellow solution was changed to brown. The brown solution was concentrated to about 10 ml under reduced pressure and diethyl ether (10 ml) was added to isolate a pale brown complex as precipitate. It was centrifuged and washed with diethyl ether followed by recrystallizing twice from acetonitrile-ether and drying in vacuum (m.p. 158-160°C) (yield, ~48%).

Anal. Calcd. for $[\text{CoH}(\text{P}(\text{OPh})_3)_2(\text{NSA})]$: C, 61.5; H, 4.4; N, 1.7; S, 3.9; Co, 7.2. Found: C, 61.4; H, 4.1; N, 2.0; S, 4.2; Co, 7.0%.

(6) Chloro(triphenylphosphine)bis(N-sulphinylaniline)rhodium(I)

Chlorotris(triphenylphosphine)rhodium(I) (0.46 g, ~0.5 mmole) in dichloromethane (15 ml) was gradually added to a solution (10 ml) of the ligand, NSA (0.5 ml, ~3 mmole) in benzene and refluxed for two hours over a water-bath. The resulting solution was concentrated to about 10 ml under reduced pressure. A light brown complex was precipitated by the addition of petroleum ether (10 ml). It was centrifuged, washed with petroleum ether for a few times and dried in a vacuum desiccator (m.p. 210-212°C) (yield, ~60%).

Anal. Calcd. for $[\text{RhCl}(\text{PPh}_3)(\text{NSA})_2]$: C, 53.0; H, 3.7; N, 4.1; S, 9.4; Cl, 5.3. Found: C, 53.3; H, 3.5; N, 4.4; S, 9.8; Cl, 5.6% .

(7) Carbonylchloro(triphenylphosphine)(N-sulphinylaniline)-rhodium(I)

To a stirred benzene solution (10 ml) of carbonylchlorobis(triphenylphosphine)rhodium(I) (~ 0.5 mmole) the ligand, NSA (0.5 ml, 3 mmole) in 8 ml of benzene was gradually added under nitrogen atmosphere. Stirring was continued for another one hour and the brown solution was concentrated to about 10 ml under low pressure. Addition of about 10 ml of petroleum ether ($60-80^\circ$) to it precipitated a yellowish brown complex which was centrifuged, washed with petroleum ether. The complex was recrystallized by dissolving it in the minimum amount of benzene, followed by an addition of petroleum ether. The recrystallization process was repeated several times until a constant melting complex was obtained (m.p. $238-240^\circ\text{C}$) (yield, 68%).

Anal. Calcd. for $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)(\text{NSA})]$: C, 52.8; H, 3.5; N, 2.5; S, 5.6; Cl, 6.3. Found: C, 52.4; H, 3.3; N, 2.8; S, 5.2; Cl, 6.4%.

(8) Bis(triphenylphosphite)bis(N-sulphinylaniline)nickel(0)

A solution of tetrakis(triphenylphosphite)nickel(0) (1.3 g, ~ 1 mmole) in chloroform (15 ml) was refluxed with a benzene solution (10 ml) of the ligand, NSA (1 ml, ~ 6 mmole) for about

two hrs. On cooling the resulting red-brown solution, a brown compound got settled down which was centrifuged, washed with a benzene-petroleum ether (1:3) solution for a few times and dried in vacuum (m.p. 169-170°C)(yield, ~38%).

Anal. Calcd. for $[\text{Ni}(\text{P}(\text{OPh})_3)_2(\text{NSA})_2]$: C, 60.2; H, 4.2; N, 2.9; S, 6.7; Ni, 6.2. Found: C, 59.6; H, 4.0; N, 3.3; S, 6.9; Ni, 6.0%.

(9) Bis(triphenylphosphine)bis(N-sulphonylaniline)palladium(0)

Tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.5 mmole) was dissolved in benzene (15 ml) under pure dry nitrogen atmosphere and kept magnetically stirred. 0.5 ml (3 mmole) of the ligand, NSA in 10 ml of benzene was gradually added and the stirring was continued for one more hour. The resulting red-orange solution was concentrated to about 10 ml under reduced pressure. On addition of petroleum ether (15 ml) to the solution, an orange complex was precipitated which was centrifuged and washed with alcohol and ether. It was recrystallized from benzene-petroleum ether (1:3), dried and kept under vacuum desiccation (m.p. 138-140°C)(yield, ~55%).

Anal. Calcd. for $[\text{Pd}(\text{PPh}_3)_2(\text{NSA})_2]$: C, 63.4; H, 4.4; N, 3.1; S, 7.1; Pd, 11.7. Found: C, 63.2; H, 4.0; N, 3.4; S, 7.4; Pd, 11.6%.

(10) Bis(triphenylphosphine)bis(N-sulphonylaniline)platinum(0)

The procedure followed to prepare the complex was the same as that given in (9), except that $\text{Pt}(\text{PPh}_3)_4$ was taken in the place of $\text{Pd}(\text{PPh}_3)_4$. A pale yellow compound (m.p. $172-173^\circ\text{C}$) was obtained (yield, $\sim 60\%$).

Anal. Calcd. for $[\text{Pt}(\text{PPh}_3)_2(\text{NSA})_2]$: C, 57.8; H, 4.0; N, 2.8; S, 6.4. Found: C, 57.5; H, 4.1; N, 3.0; S, 6.6%.

(11) Monochlorobis(triphenylphosphine)(N-sulphonylaniline)-copper(I)

$\text{CuCl}(\text{PPh}_3)_3$ (1.8 g, ~ 2 mmole) was dissolved with stirring in 20 ml of dichloromethane and a solution of the ligand, NSA (2 ml, ~ 13 mmole) in dichloromethane (10 ml) was slowly added to it. The stirring was further continued for 1.5 hours. The resulting brown solution was concentrated to about 10 ml over a water-bath and a pale yellow complex was precipitated by an addition of about 10 ml of petroleum ether ($60-80^\circ$). It was centrifuged and washed with n-pentane. It was then recrystallized twice from dichloromethane-petroleum ether and dried in a vacuum desiccator (m.p. $220-223^\circ\text{C}$) (yield, $\sim 43\%$).

Anal. Calcd. for $[\text{CuCl}(\text{PPh}_3)_2(\text{NSA})]$: C, 66.1; H, 4.6; N, 1.8; S, 4.2; Cl, 4.7; Cu, 8.4. Found: C, 65.8; H, 4.2; N, 2.0; S, 4.4; Cl, 5.0; Cu, 8.3%.

(12) (Triphenylphosphine)(N-sulphonylaniline)silver(I) nitrate

$[Ag(PPh_3)_4](NO_3)$ (1.2 g, ~ 1 mmole) was dissolved in 15 ml of acetonitrile and refluxed with a solution of the ligand, NSA (0.6 ml, ~ 5 mmole) in acetonitrile (10 ml) for an hour. During the course of refluxing, the colour of the yellow solution slowly changed to red-brown. On slow cooling and leaving for 2-3 hours, a grey coloured compound got settled down. It was centrifuged, washed with diethyl ether and recrystallized twice from acetonitrile-ether (m.p. $> 300^\circ C$) (yield, $\sim 38\%$).

Anal. Calcd. for $[Ag(PPh_3)(NSA)](NO_3)$: C, 50.4; H, 3.5; N, 4.9; S, 5.6; Ag, 18.9. Found: C, 50.1; H, 3.3; N, 5.1; S, 5.7; Ag, 18.7%.

Analyses

Elemental analyses were performed by the methods described in Chapters II and III. Infrared, magnetic susceptibility and the electronic spectra of the ligand and complexes were taken by the procedures followed in Chapter II. The major bands of infrared spectra and their assignments are given in Table IV.1. Magnetic moments, the positions and the assignments of bands in the electronic spectra of the ligand and complexes are given in Table IV.2.

RESULTS AND DISCUSSION

The analytical data correspond to the empirical formulas which suggest that the ligand is behaving as monodentate in all the complexes, if the preferential geometries which the metal ions adopt in their complexes are assumed [12a]. Since the complexes have been found to be soluble in the organic solvents, it is assumed that they are monomeric in nature.

The ligand has four preferential sites for the metal bonding: (1) phenyl group as a whole which can form π -type of complexes with the metal ions by the overlap of π -orbitals of the phenyl group with metal d-orbitals; (2) oxygen, sulphur and nitrogen atoms which can form complexes by the overlap of orbitals having paired non-bonding electrons with the appropriate metal orbitals. However, it is unlikely that the phenyl filled π -orbitals and oxygen lone pair will take part in the bond formation because of their relatively very low energies, as compared to those of nitrogen and sulphur [1]. It is, therefore, assumed that the bonding of the ligand molecule with the metal ions will take place either with nitrogen or with sulphur atom. In order to decide between these two alternatives, the infrared spectra of the ligand and its complexes were studied.

The infrared spectrum of the ligand has been studied in detail by Stephenson, et al. [13] by assuming the molecule having C_s symmetry. We have followed the assignments as given

by them. Table IV.1 contains the major spectral data and their assignments. Besides the characteristic bands of the phenyl group present in the spectra of the ligand and the complexes, the spectrum showed two strong bands at 1158 cm^{-1} and 1298 cm^{-1} which have been assigned to the two stretching vibrations of -NSO group and the bands at 606 cm^{-1} , 438 cm^{-1} and 411 cm^{-1} are assigned to -NSO inplane bending, -NSO out-of-plane bending and -NSO inplane wagging modes, respectively [13]. Further, the spectra of substituted phenyl analogues have also been studied and discussed by Kresze and Maschke [14]. They have shown: (1) that the -NSO group has, atleast in the N-S bond, an easily polarizable system, (2) that the N-S bond may be considered as double bond which may enter into conjugation with the π -electron system of the phenyl ring and groups which can act as donors, thereby lowering the N-S bond order and (3) that acceptor groups as substituents, at the N-atom, increase the bond order of N-S. Thus, it may be concluded that the phenyl π -electrons should be in conjugation with the π -electrons of -NSO group and in the stretching vibrational modes of the -NSO, the normal coordinates which give rise to these bands in the infrared spectrum must also have a fair amount of contribution from (C=N) and (C=C) stretching modes. It is further thought that these contributions should be relatively more in the normal coordinate giving rise to 1298 cm^{-1} band than that to 1177 cm^{-1} band having more contribution from $\nu(\text{SO})$, $\nu(\text{N=S})$ and other stretching modes of -NSO. In metal complexes, when the metal

ions (electron acceptors) interact with the nitrogen lone pairs, the contributions from the vibrational modes of C=N and N=S should therefore increase in the normal coordinates because of which the various bands of -NSO in the spectra are obtained. Thus, it is expected that on complexation, the position of the band at 1298 cm^{-1} should shift towards the higher wave numbers, while that of 1158 cm^{-1} band should shift towards lower wave numbers. The positions of the bands arising due to other bending modes should be slightly shifted. In addition, since the phenyl group is also participating in the resonating structures, all the bands arising due to phenyl skeletal modes of vibration should also be shifted towards higher wave numbers. The following are the major shifts in the band positions of -NSO and some of those of the phenyl group:

(a) In the ligand spectrum, the bands assigned to phenyl group were present at 1600, 1570, 1483, 1451, 1330, 1071, 1032, 1016, 998, 763, 750 & 682 cm^{-1} [12,13]. The positions of the bands at 1600, 1570, 1483, 1451 & 1330 cm^{-1} have been shifted towards higher wave numbers ($+10\text{ cm}^{-1}$), those at 1071, 1032, 1016, 998, 763, 750 & 682 cm^{-1} were not shifted and the shifts in the positions of the remaining phenyl bands at lower wave numbers were relatively small and variable ($\pm 5\text{ cm}^{-1}$). It indicated that possibly the positions of only those bands are shifted which have some contribution from $\nu(\text{C}=\text{C})$ vibrational mode and the positions of those which have contributions from

C-H vibrational mode did not change. It is in conformity with the discussion in the foregoing paragraph.

(b) The position of the band at 1298 cm^{-1} shifted towards higher wave numbers ($\sim +15\text{ cm}^{-1}$) in the spectra of all the complexes, suggesting the bonding of metal ions with the nitrogen atom of the -NSO group.

(c) The position of the band at 1158 cm^{-1} shifted towards lower wave numbers, ($\sim -20\text{ cm}^{-1}$) in the spectra of all the complexes.

(d) The shifts in the positions of the bands at 636 cm^{-1} , 505 cm^{-1} and 438 cm^{-1} in the spectra of the complexes could not be ascertained because of the presence of other weak and medium intensity bands in this region. However, in a number of spectra, 636 cm^{-1} band position appeared to have shifted towards lower wave numbers ($\sim 10\text{ cm}^{-1}$).

(e) All the characteristic bands of triphenylphosphine were present in the spectra of the complexes of iron, ruthenium, rhodium, nickel, palladium, platinum, copper and silver. Further, the spectra of $[\text{RuCl}_2(\text{AsPh}_3)_2(\text{NSA})_2]$ and $[\text{CoH}(\text{P}(\text{OPh})_3)_2(\text{NSA})]$ exhibited the characteristic bands of triphenylarsine and triphenylphosphite, respectively.

(f) The spectrum of $[\text{Ag}(\text{PPh}_3)(\text{NSA})](\text{NO}_3)$ showed all the characteristic bands of nitrate group.

(g) In the spectrum of $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)(\text{NSA})]$, there appeared a band at 1960 cm^{-1} assigned to $\nu(\text{CO})$.

It is, therefore, concluded that the ligand is bonded with the metal ion through its nitrogen atom and is acting as monodentate.

Magnetic Moment

The complexes of Ru(II), Rh(I), Co(I), Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I) were found to be diamagnetic (Table IV.2) in nature at room temperature. The diamagnetic behaviour of ruthenium(II) complexes clearly reveals that the metal ion exists as low spin d^6 system in both the complexes. In general, all the octahedral complexes of ruthenium(II), known till now, are diamagnetic [12b] and therefore an octahedral geometry has been assigned to the complex. The diamagnetic behaviour of cobalt(I) and rhodium(I) (both belong to d^8 system) indicates the square planar geometry around the metal ions which is the preferred geometry of these metal ions in their complexes [12c].

The diamagnetic nature of palladium(0), platinum(0), nickel(0), copper(I) and silver(I) complexes leads to plausible conclusion that the metal ions in their complexes belong to d^{10} system. Since palladium(0), platinum(0), nickel(0) and copper(I) complexes are four coordinated, the only possible geometry that may be assigned to them is tetrahedral, which is in conformity with the one known in the literature for the four coordinated complexes of metal ions having d^{10} system [12d]. The coordination number in the silver complex could be assigned

as two (if NO_3^- ion is assumed to be ionic) or three (if NO_3^- is assumed as coordinated). Since the complex is insoluble in water, its conductivity could not be determined and it is hard to know the nature of bonding of silver ion with the nitrate group. Under both alternatives, the 4d-orbital of silver ion is completely filled and therefore, one should expect the diamagnetic nature of the complex. In general, silver forms linear complexes with coordination number two, it is therefore assumed that the silver complex is two coordinated with nitrate ion as ionic in nature. However, the possibility of the presence of tricoordinated silver ion also exists with nitrate forming coordinate bond. Nitrate ion acting as a bidentate in the complex is ruled out on the basis of infrared studies (the positions of the NO_3^- bands did not correspond to the one expected for bicoordinated NO_3^- ion).

The complex of iron(II) was found to be paramagnetic and exhibited 5.1 B.M. (μ value) which is slightly higher than that corresponding to four unpaired electrons. The slightly higher value may possibly be due to some orbital contribution to the spin only value of the magnetic moment. The theoretical value for high spin d^6 system using ligand field theory [15] μ should correspond to 5.2 B.M. (using $10 Dq \cong 4000 \text{ cm}^{-1}$). The experimental value corresponds very well with the theoretical one. Further, since the number of ligands around iron(II) ion in its complex is four, it is presumed that iron(II) forms four coordinated tetrahedral high spin complex with NSA having triphenylphosphine and chloride ions as coligands.

The magnetic moment value of manganese was found to be 5.8 B.M. which suggested manganese to be present in +2 oxidation state with five unpaired electrons. Since the ground state of Mn(II) ion is non-degenerate, the orbital contribution should be practically zero. The spin only value of high spin d^5 system should correspond to about 5.9 B.M. A slight low experimental value (5.8 B.M.) of the complex may be due to some experimental error. However, the value of magnetic moment indicates the presence of five unpaired electrons. Since the analytical data suggest four monodentate ligands around the manganese ion, a tetrahedral geometry is assumed on the basis of magnetic data.

Electronic Spectra

The electronic spectra of the ligand and complexes are shown in Fig. IV.2. The near ultraviolet spectrum of the ligand showed two absorption bands at 320 nm (31250 cm^{-1} , $\log \epsilon = 3.90$) and 235 nm (42553 cm^{-1} , $\log \epsilon = 3.80$). The spectrum has been analysed by Leandri and Mangini [16], who have assigned the low energy band to $n_{\text{nitrogen}} \rightarrow \pi^*$ and the high energy one to $n_{\text{sulphur}} \rightarrow \pi^*$ transitions. Their assignments have been based on the comparative study of the electronic spectra of SO_2 and various aromatic and aliphatic thionylamines. In thionylamines, the bands were assigned in the reverse order as those of the bands observed in SO_2 . The reasons for doing so are as follows: (a) Replacing one of the oxygen atoms of SO_2 by R-N group, the non-bonding orbital on oxygen in SO_2 will become partially nitrogen orbital

which will be higher in energy, even above the lone pair of sulphur orbitals and (b) the anti-bonding orbital (π^*) will be considerably raised because the reduced electronegativity difference between sulphur and nitrogen will cause the π^* -orbital which is concentrated on sulphur in SO_2 to become better distributed over nitrogen and sulphur and therefore, there will be stronger repulsion between these two atoms. If one presumes that the bonding of the metal ion in the complexes takes place with the non-bonding lone pair on nitrogen atom by removing a part of the negative charge from nitrogen atom, the effective electronegativity of nitrogen will be slightly raised and the lone pair of nitrogen will be more delocalized over the nitrogen and metal centres. It will result in the stabilization of the non-bonding orbitals by lowering their energy, which will cause greater energy difference between non-bonding orbital of nitrogen and those of the π^* orbitals of -NSO group. This will make the position of the 320 nm band shift towards shorter wave length side. On the other hand, if the bonding of the metal ions is assumed to be through sulphur atom of -NSO group, the non-bonding electrons on sulphur atom will be more stabilized and thus shifting the position of the band due to $n_{\text{sulphur}} \rightarrow \pi^*$ transition towards shorter wave length will be expected. Experimentally it is observed that the position of band due to $n_{\text{nitrogen}} \rightarrow \pi^*$ transition has been shifted to lower wave length (~ 10 nm) and therefore bonding of the metal ion is assumed with the nitrogen atom of the ligand.

In the spectra of those complexes having triphenylphosphine or triphenylarsine as coligand, one or two bands in the 270 nm region have been observed. These are characteristic $\pi \rightarrow \pi^*$ transition bands of the phenyl groups of phosphine. The splitting of this band into two may be due to interligand interaction of the π or π^* levels.

In the spectra of all the complexes, a continuous intense absorption started from 550 nm downward. The very high intensity of this absorption suggests that they should be charge transfer bands and not due to d-d transition. This absorption may either arise due to charge transfer or may be intraligand band. Since the continuous absorption was observed in the spectra of those of d^{10} system, as well as that in the ligand spectra, it is assumed that the continuous absorption is due to intraligand transition.

All the d-d transition bands appearing in lower wave length region than 500 nm (20000 cm^{-1}) were masked by the intense continuous absorption by the ligand and hence no d-d transition bands were observed in the spectra of the complexes. However, a weak band appeared at 550 nm in the spectrum of Ru(II) arsine complex. This has been assigned to $^1T_{2g} \rightarrow ^1A_{1g}$ transition, indicating the octahedral geometry [17]. No information regarding the stereochemistry of other complexes could therefore be inferred from the visible spectral data. In addition, one also does not expect any band in the visible range of the spectrum in the case of d^{10} system.

Thus, from the analytical, magnetic and spectral (i.r., u.v. and visible) data, the following tentative geometries of the complexes are postulated with the bonding through nitrogen atom of the ligand:

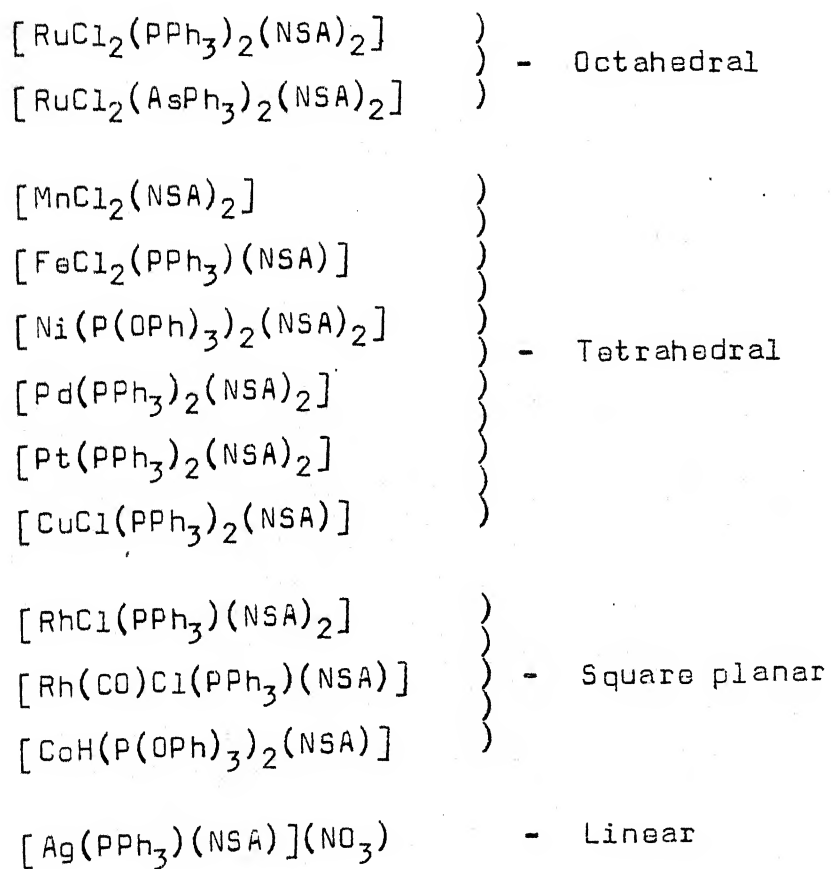


Table IV.1

Major Infrared Bands of the Ligand and its
Complexes with Their Assignments

NSA (cm^{-1})	Complexes (cm^{-1})	Assignments
1298(s)	$\sim 1313(\text{m})$	$\nu(\text{NSO})$
1158(s)	$\sim 1138(\text{m})$	$\nu(\text{NSO})$
606(m)		$\delta(\text{NSO})$ (in plane)
438(m)		$\delta(\text{NSO})$ (out of plane)
411(w)		$\omega(\text{NSO})$ (in plane)
636(s)	$630(\pm 5)(\text{m})$	Not assigned because of other bands in this region
505(m)	Variable	
438(m)	shifts	
1600(s), 1570(m), 1483(s), 1451(m), 1330(m)	Shifted towards higher wave numbers ($\sim 10 \text{ cm}^{-1}$)	Characteristic bands of phenyl group
1071(m), 1032(m), 1016(m), 998(m), 763(s), 750(m), 682(s)	Not shifted	
-	1960(vs)	$\nu(\text{CO})$ of [Rh(CO)Cl(PPh ₃)(NSA)]

(s), strong; (m), medium; (w), weak; (vs), very strong.

Table IV.2

Magnetic Moments, Electronic Absorption Bands of the Ligand, Complexes and Their Assignments

Compounds	Band positions nm (cm ⁻¹)	Assignments	Magnetic Moments (B.M.)
NSA	320 (31,250) 235 (42,553)	n(nitrogen) → π* n(sulphur) → π*	
PPh ₃ or AsPh ₃ Complexes	270 (37,037) 550 (18,182) (intense)	π → π* of the phenyl groups IL	
[RuCl ₂ (AsPh ₃) ₂ (NSA) ₂]	550 (18,182) (weak)	¹ T _{2g} → ¹ A _{1g}	DM
[MnCl ₂ (NSA) ₂]	-	-	5.8
[FeCl ₂ (PPh ₃)(NSA)]	-	-	5.1

IL, intraligand; DM, diamagnetic

LEGEND TO THE FIGURES

Fig. IV.1 Infrared Spectra of NSA and its Complexes

- (1) NSA
- (2) $[\text{MnCl}_2(\text{NSA})_2]$
- (3) $[\text{FeCl}_2(\text{PPh}_3)(\text{NSA})]$
- (4) $[\text{RuCl}_2(\text{PPh}_3)_2(\text{NSA})_2]$
- (5) $[\text{RuCl}_2(\text{AsPh}_3)_2(\text{NSA})_2]$
- (6) $[\text{CoH}(\text{P}(\text{OPh})_3)_2(\text{NSA})]$
- (7) $[\text{RhCl}(\text{PPh}_3)(\text{NSA})_2]$
- (8) $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)(\text{NSA})]$
- (9) $[\text{Ni}(\text{P}(\text{OPh})_3)_2(\text{NSA})_2]$
- (10) $[\text{Pd}(\text{PPh}_3)_2(\text{NSA})_2]$
- (11) $[\text{Pt}(\text{PPh}_3)_2(\text{NSA})_2]$
- (12) $[\text{CuCl}(\text{PPh}_3)(\text{NSA})]$
- (13) $[\text{Ag}(\text{PPh}_3)(\text{NSA})](\text{NO}_3)$

Fig. IV.2 Electronic Spectra of NSA and its Complexes

- (1) NSA
- (2) $[\text{MnCl}_2(\text{NSA})_2]$
- (3) $[\text{FeCl}_2(\text{PPh}_3)(\text{NSA})]$
- (4) $[\text{RuCl}_2(\text{PPh}_3)_2(\text{NSA})_2]$
- (5) $[\text{RuCl}_2(\text{AsPh}_3)_2(\text{NSA})_2]$
- (6) $[\text{CoH}(\text{P}(\text{OPh})_3)_2(\text{NSA})]$
- (7) $[\text{RhCl}(\text{PPh}_3)(\text{NSA})_2]$
- (8) $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)(\text{NSA})]$
- (9) $[\text{Ni}(\text{P}(\text{OPh})_3)_2(\text{NSA})_2]$
- (10) $[\text{Pd}(\text{PPh}_3)_2(\text{NSA})_2]$
- (11) $[\text{CuCl}(\text{PPh}_3)_2(\text{NSA})]$

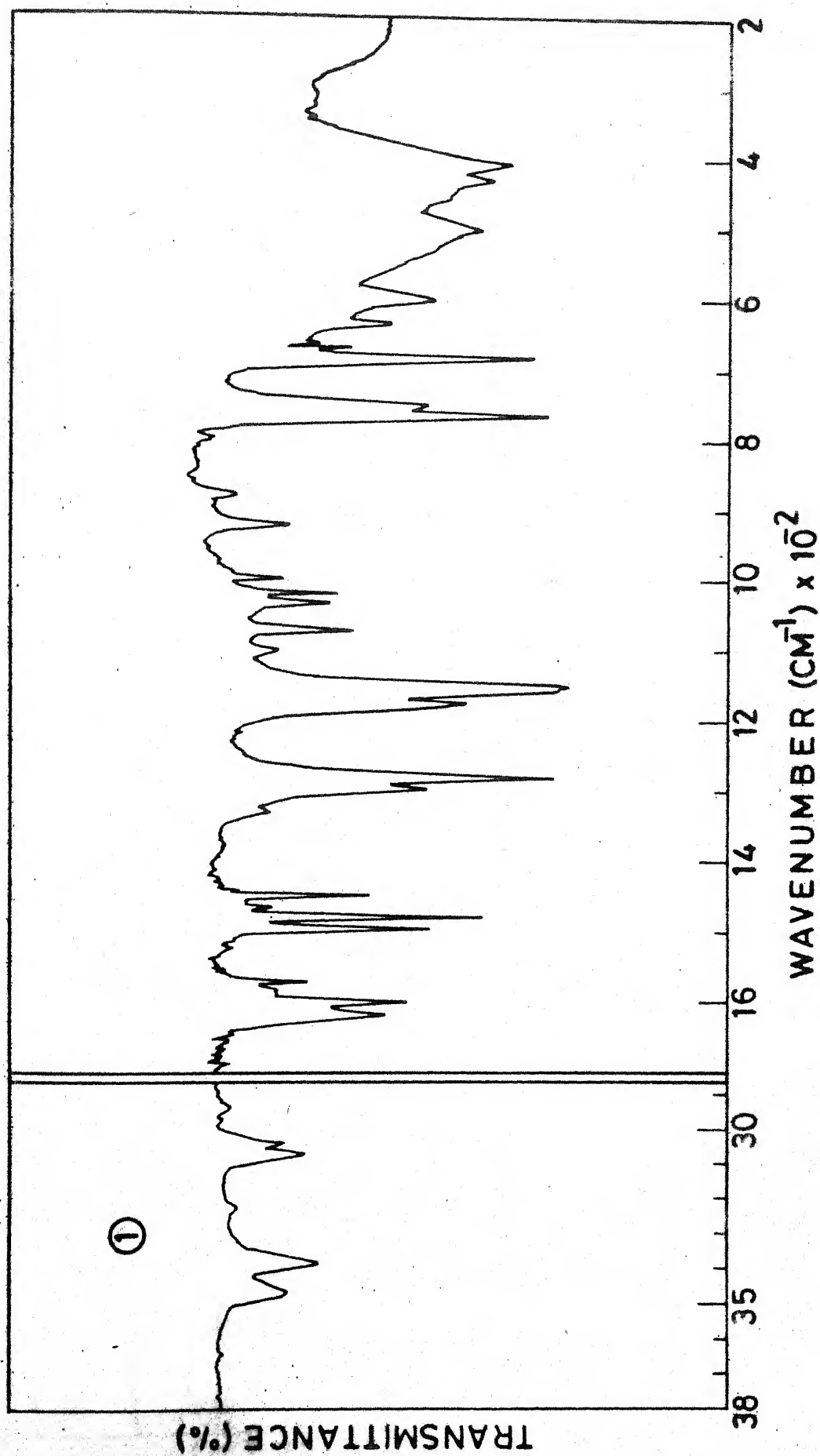


FIG. IV.1 INFRARED SPECTRUM OF ① .

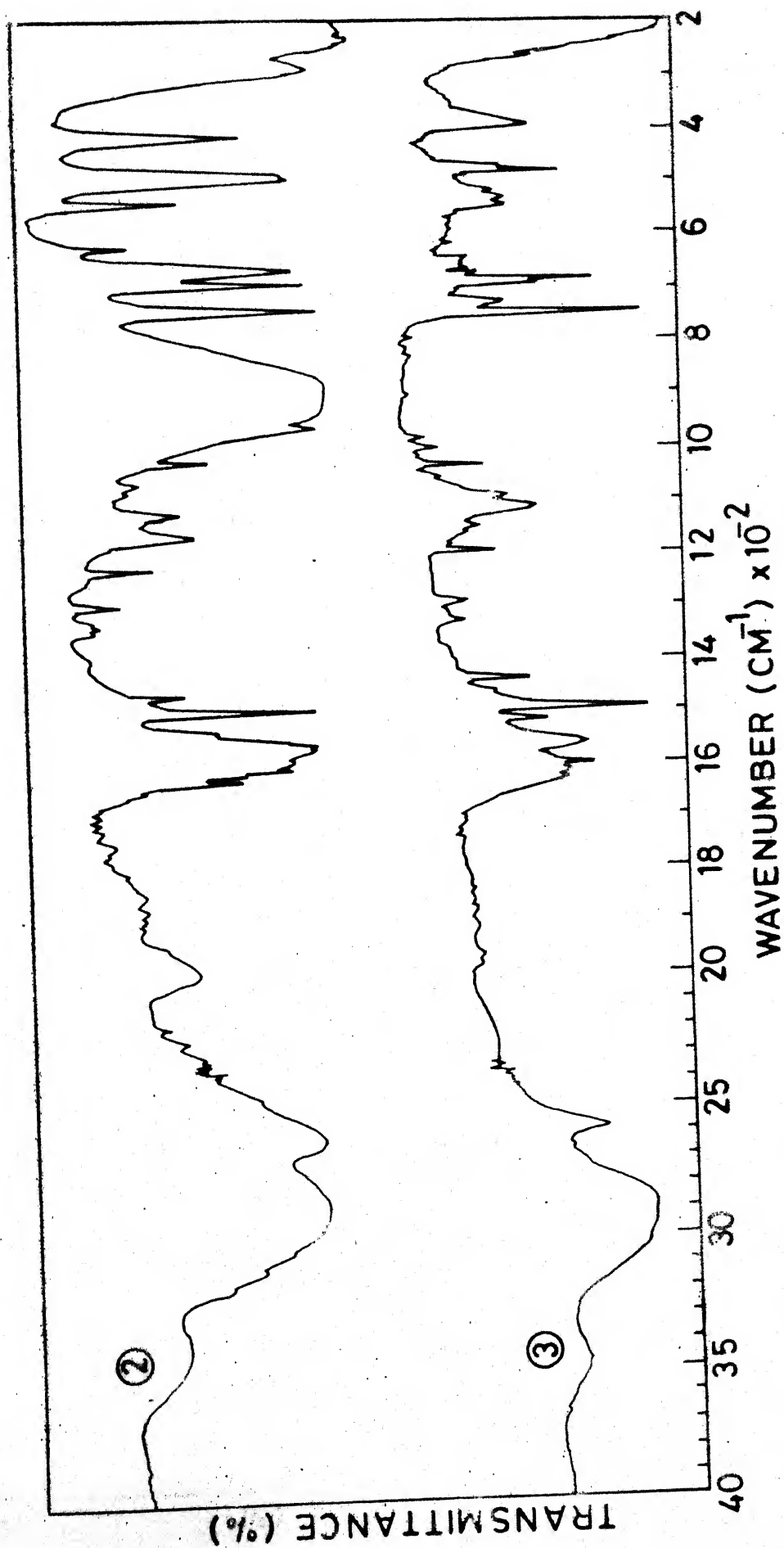


FIG. IV.1 INFRARED SPECTRA OF ② & ③

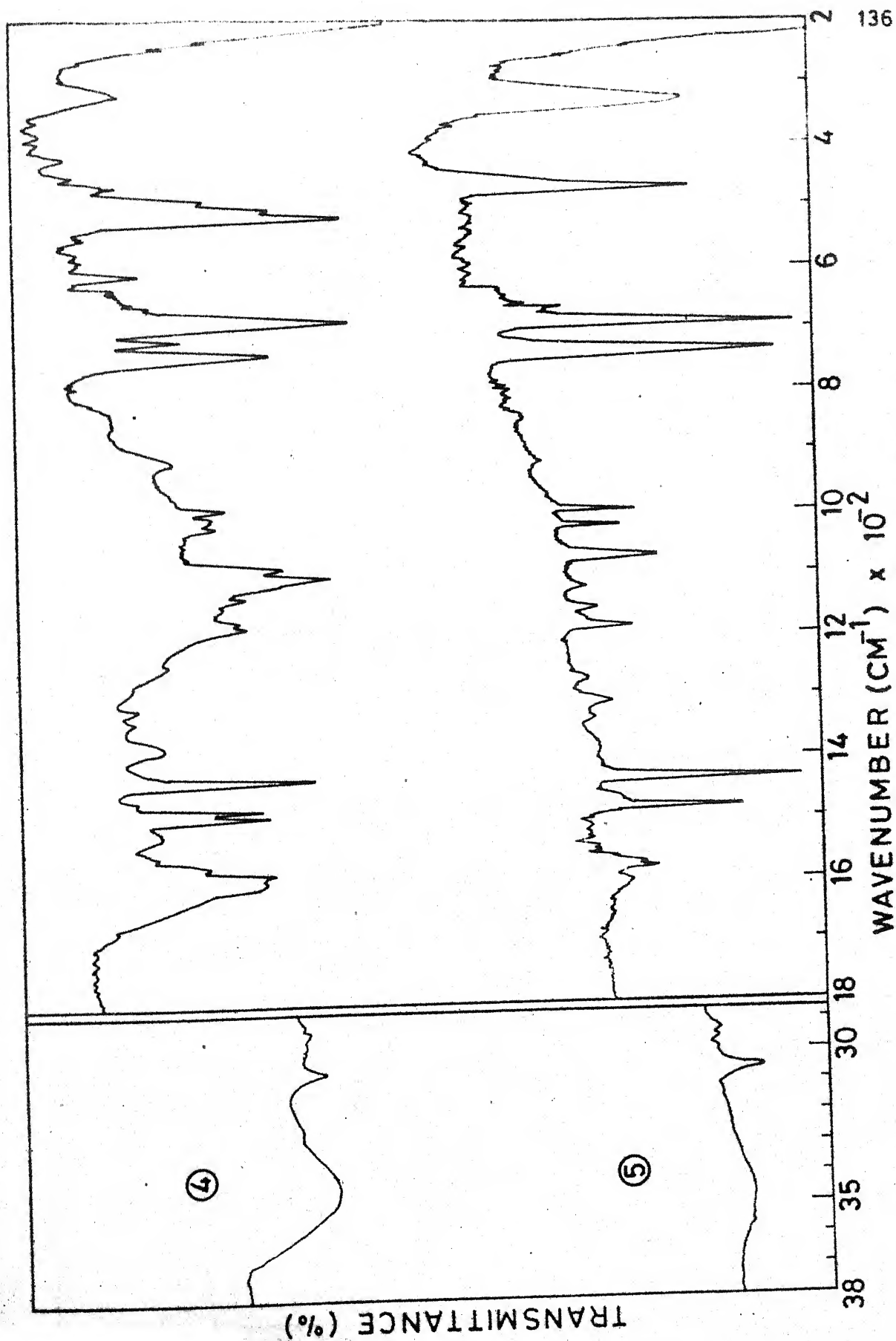


FIG. IV.1 INFRARED SPECTRA OF ④ & ⑤

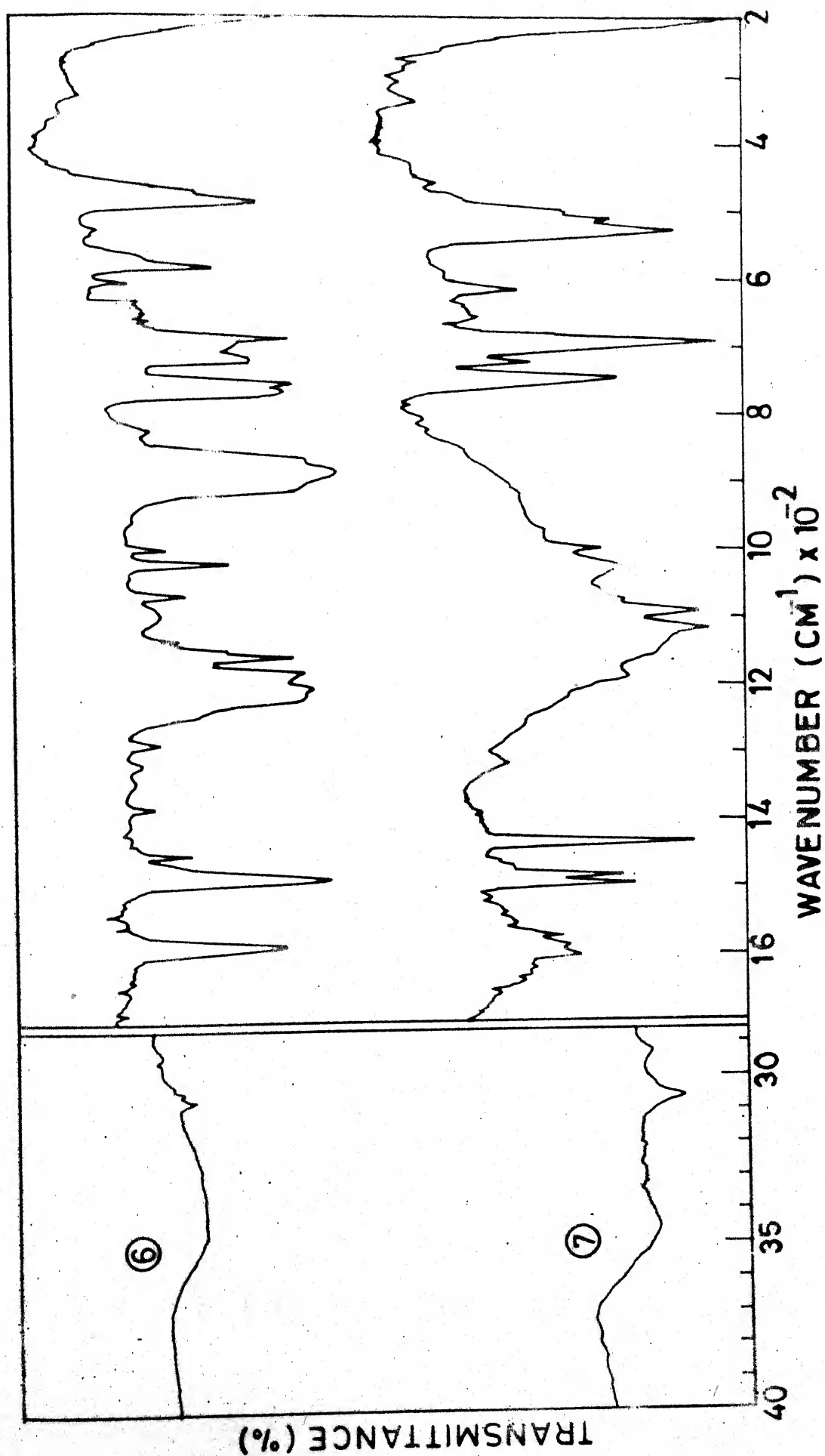


FIG. IV.1 INFRARED SPECTRA OF ⑥ & ⑦ .

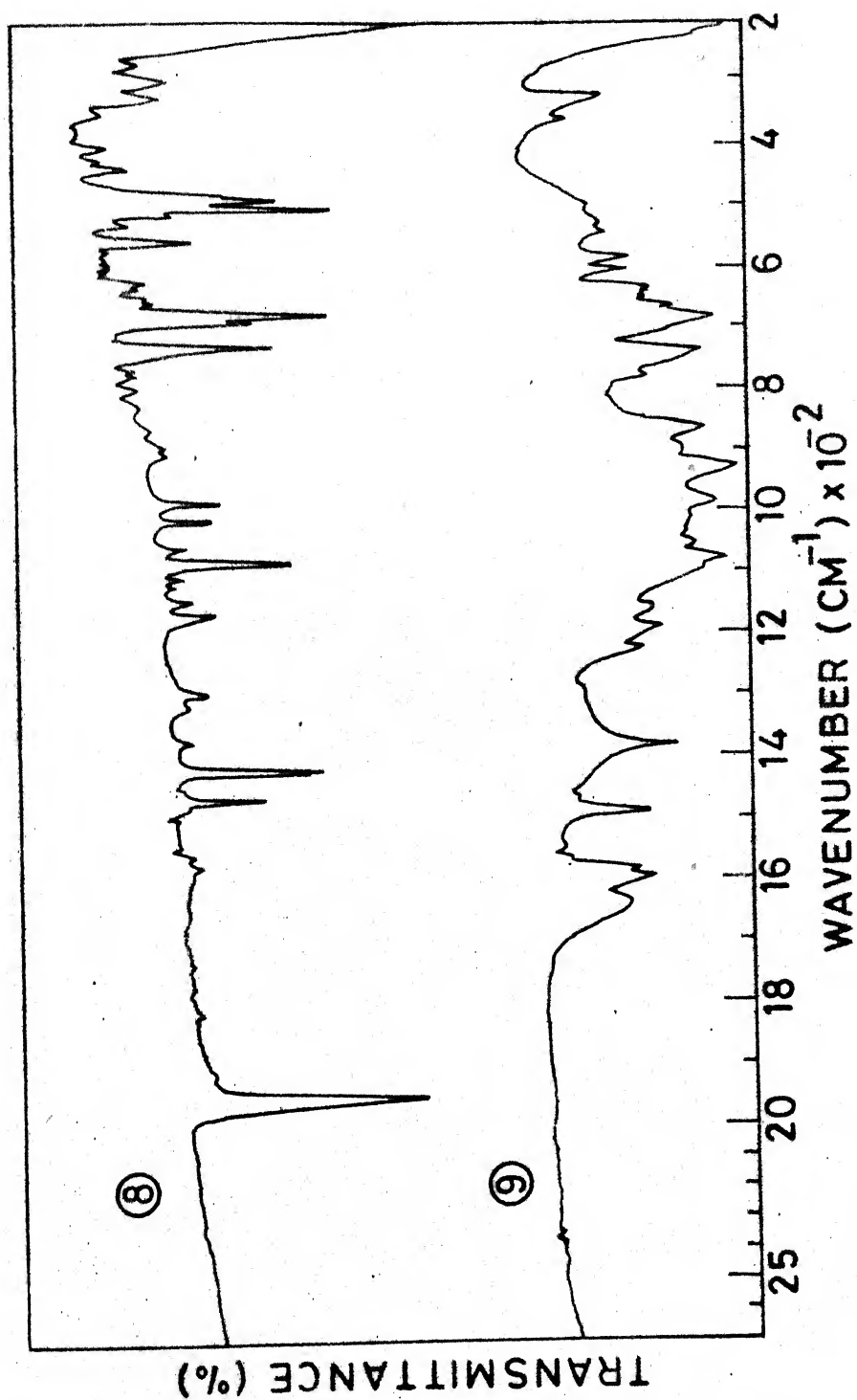


FIG. IV.1 INFRARED SPECTRA OF ⑧ & ⑨

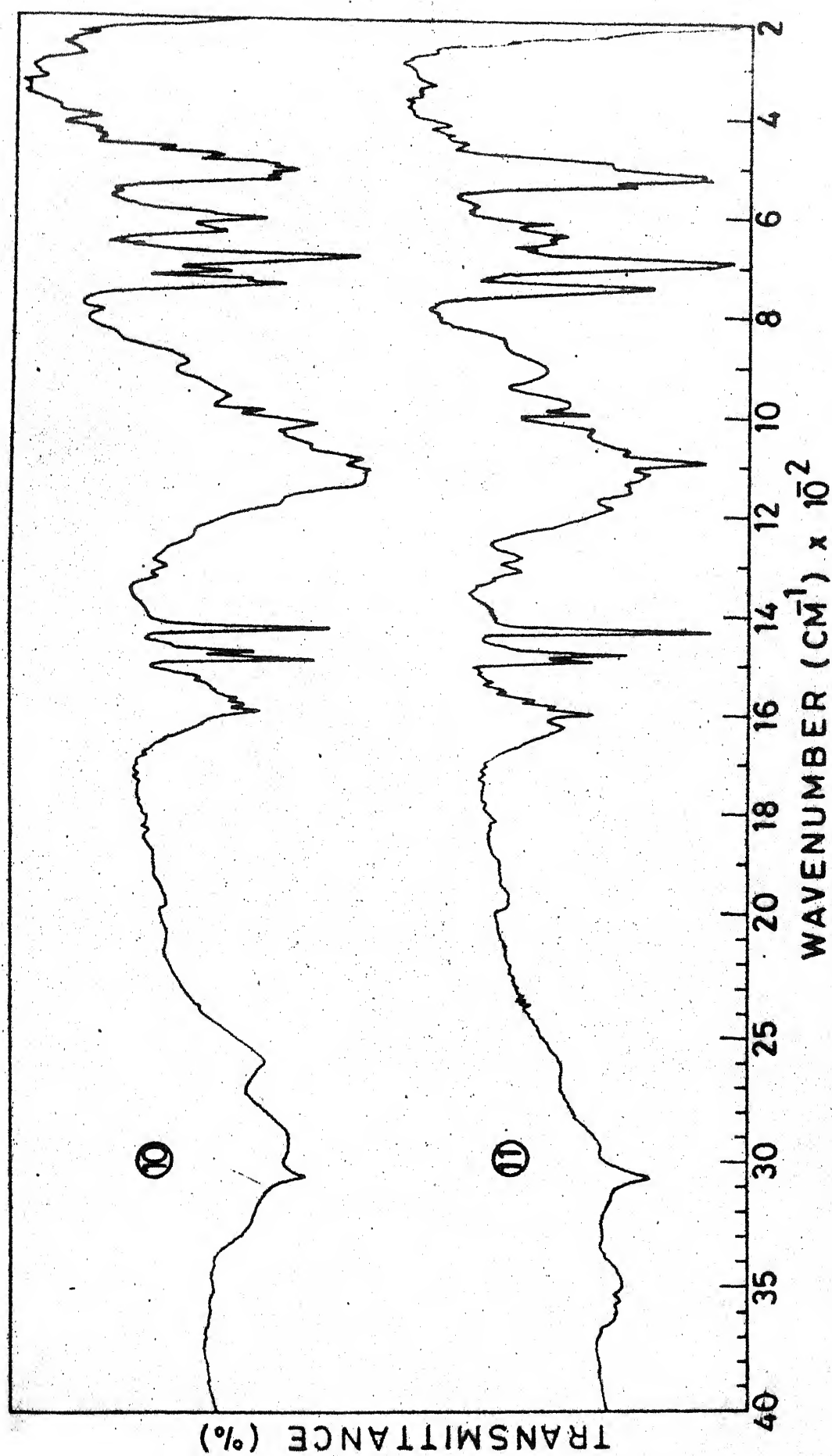


FIG. IV.1 INFRARED SPECTRA OF 10 & 11

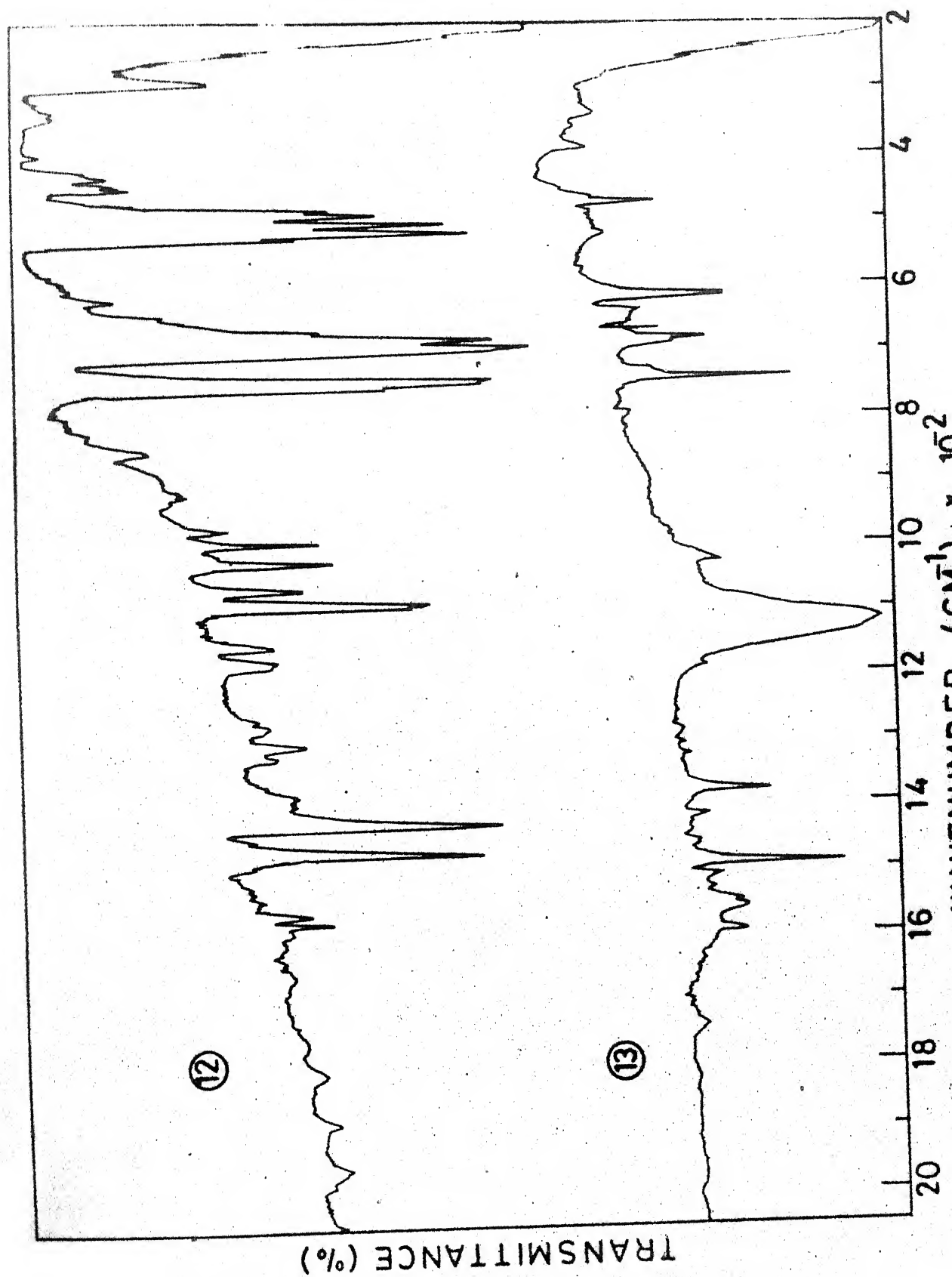


FIG. IV.1 INFRARED SPECTRA OF ⑫ & ⑬

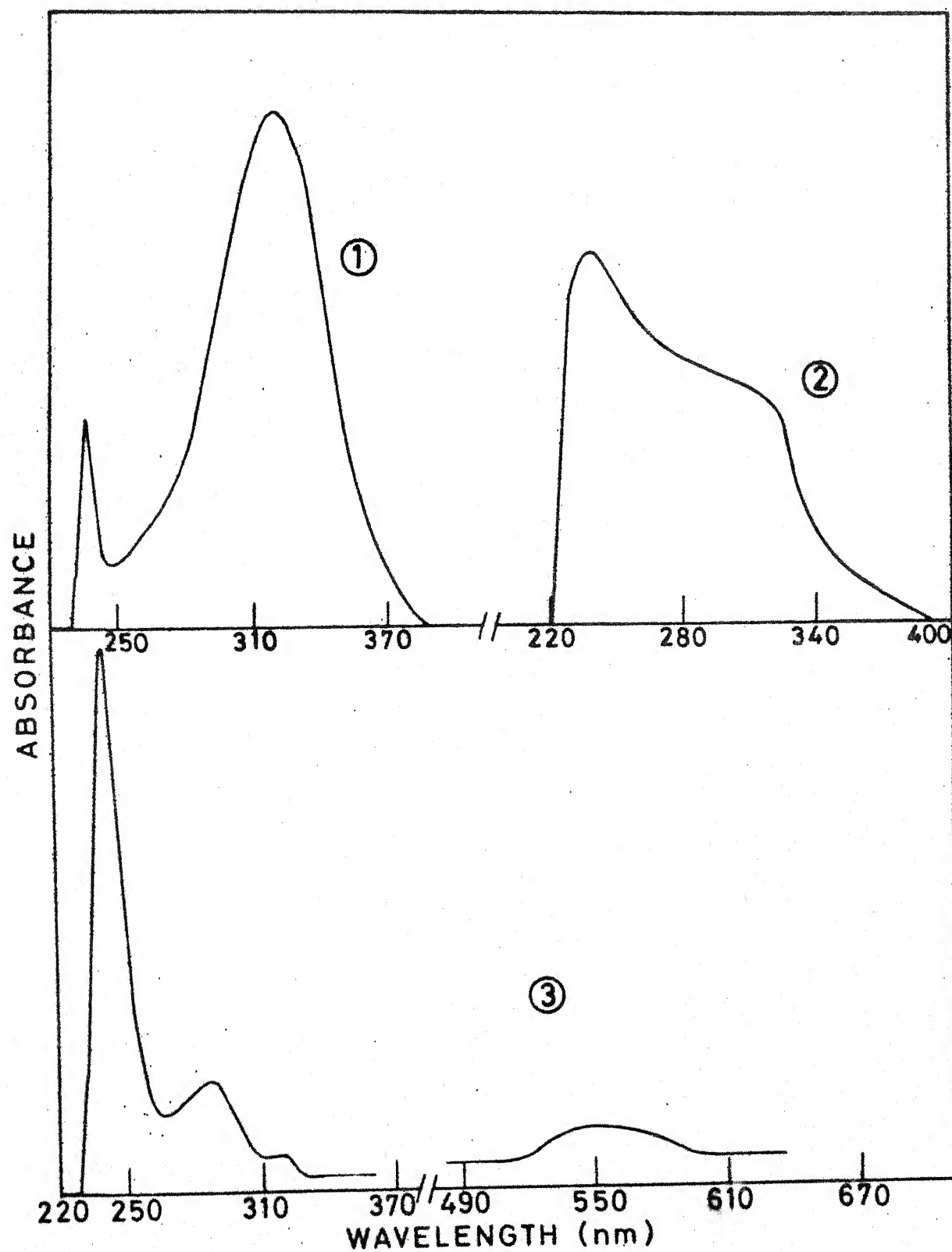


FIG. IV.2 ELECTRONIC SPECTRA OF ①, ② & ③ .

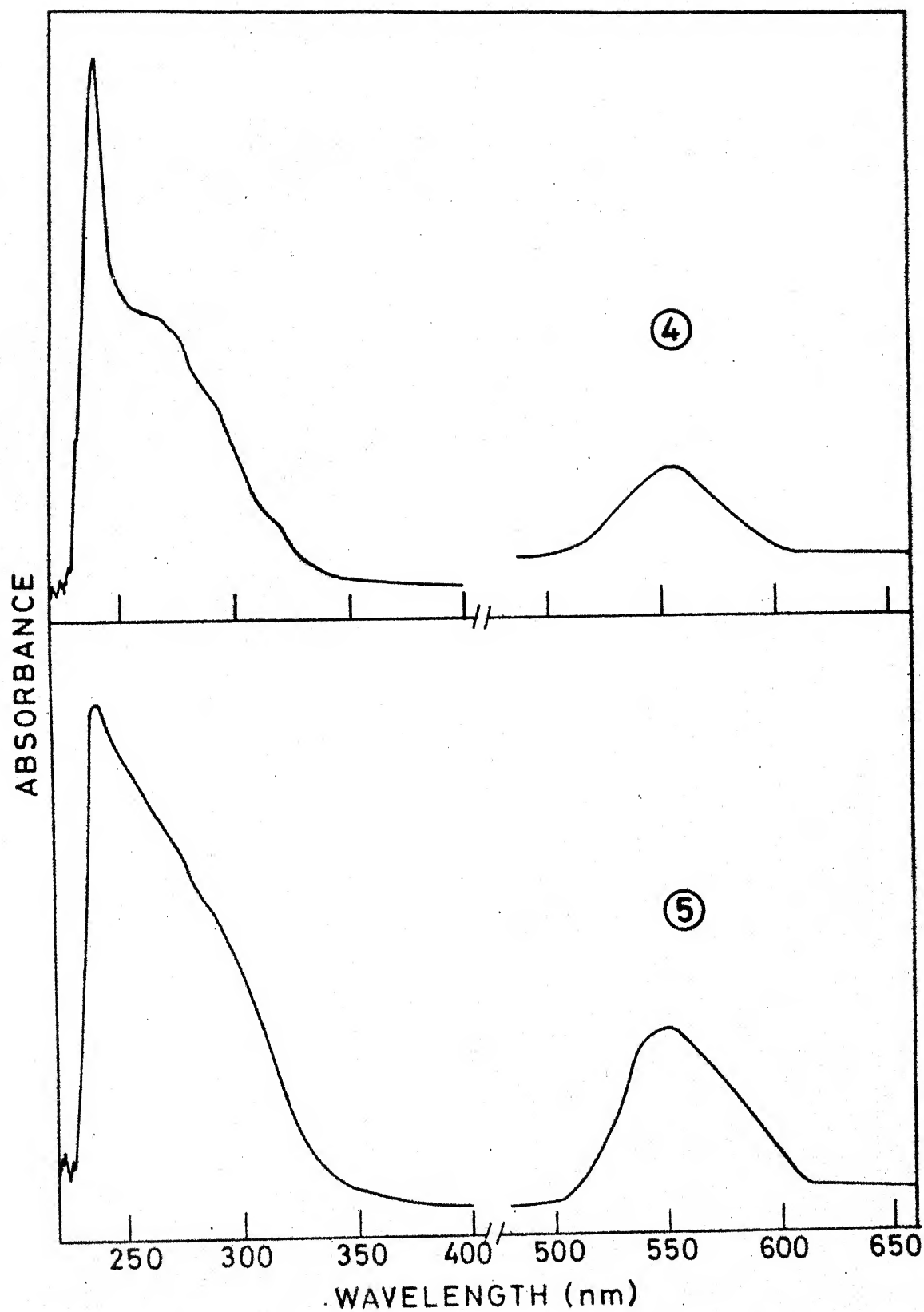


FIG. IV.2 ELECTRONIC SPECTRA OF ④ & ⑤ .

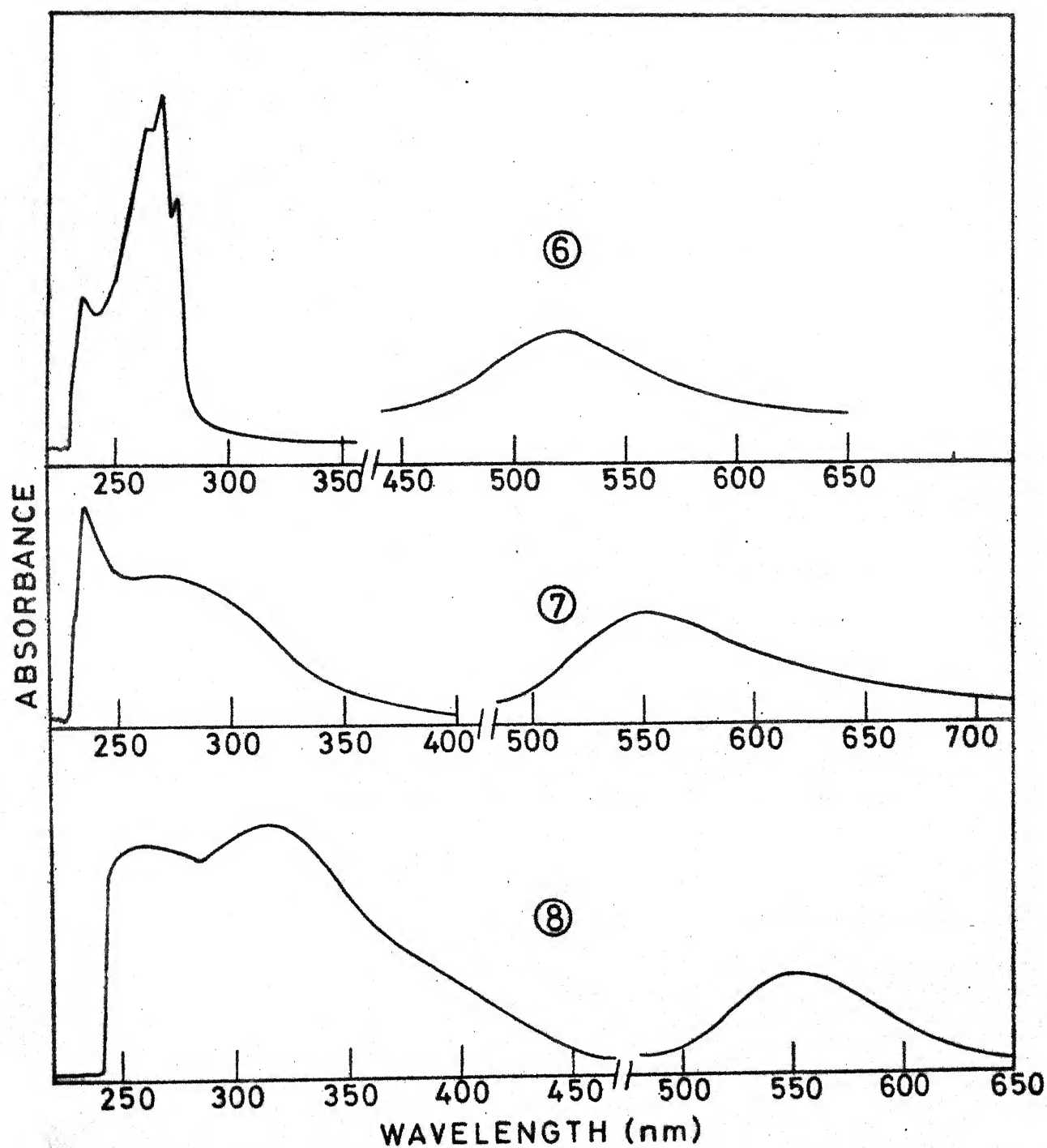


FIG. IV.2 ELECTRONIC SPECTRA OF ⑥, ⑦ & ⑧ .

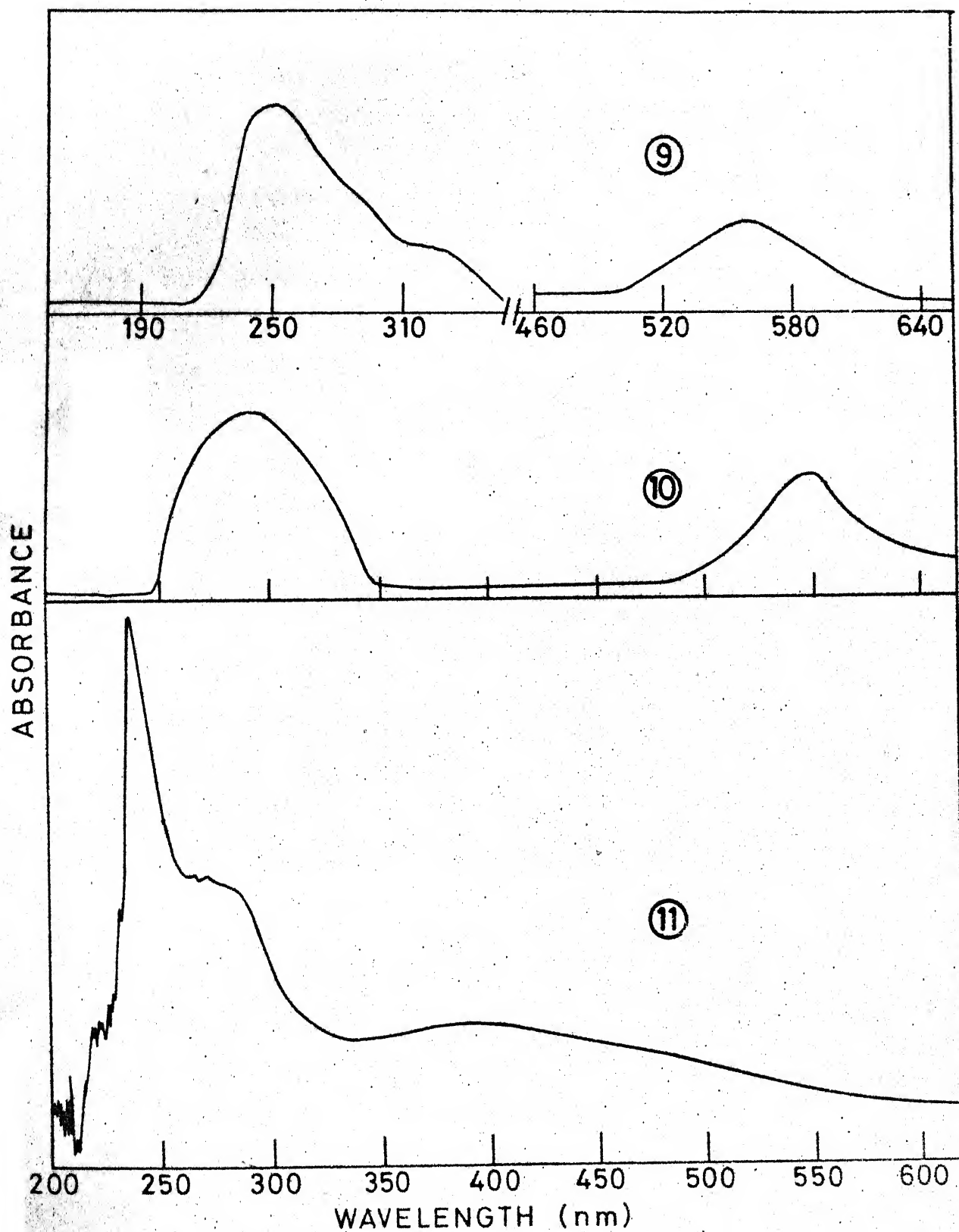


FIG. IV.2 ELECTRONIC SPECTRA OF ⑨ ⑩ & ⑪

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CHAPTER V

CHAPTER V

STABLE DIMERIC COMPLEXES WITH SULPHUR MONOXIDE: FORMATION OF $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$ (X = Cl or Br)

Despite the instability of lower oxides of sulphur, SO , $(\text{SO})_2$ and S_2O , all can be trapped as ligands [1]. The complexing properties of free sulphur monoxide, because of its very short life time (milliseconds) [2], are not known in any detail. Schmid and coworkers [3] for the first time have synthesized an Iridium complex, $[\text{Ir}(\text{SO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]\text{Cl}$ by the oxidation of $\text{cis}-(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Ir}(\text{S}_2)\text{Cl}$ with NaIO_4 . A sulphur monoxide bridging compound, $[(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{SO}$ has also been prepared [4]. Very recently, Marko, et al. [5] have been able to fix the unstable sulphur monoxide in a cluster

compound, $\text{Fe}_3(\text{CO})_9\text{S}(\text{SO})$ by the reaction of $\text{Fe}(\text{CO})_5$ and NaOH in $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1:2) with aqueous hydrogen peroxide and sodium sulphite solutions. In another report [6], claims have been made for the formation of an intermediate complex of sulphur monoxide acting as a ligand in the reduction of sulphite to sulphide using iron carbonylhydride as reductant. The supporting fact is that the S-O bond length of 147 p.m. in the compound corresponds to that in free sulphur monoxide (148 p.m.) and in many other compounds having S=O double bonds [7].

All the reported methods involve either the oxidation of metal sulphide or the reduction of sulphito compounds to get the complexes containing SO, $(\text{SO})_2$ or S_2O as ligand. It has been well known that trans-stilbene episulphoxide when taken in dichloromethane forms sulphur monoxide in the medium which may be trapped by the metal ions or their complexes. This method has already been used for the formation of organic sulphur monoxide compounds [8-11]. The present work is an attempt to prepare metal complexes with SO acting as coligand using trans-stilbene episulphoxide as a source of SO. In this chapter, the syntheses of dimeric rhodium(I) complexes with SO as ligand have been described which have been characterized by analytical, spectral, magnetic and conductivity measurements.

EXPERIMENTAL

All the reagents used were Analar or of chemically pure grade. The solvents were dried and freshly distilled before use.

Reactions were carried out under pure dry argon atmosphere.

Trans-Stilbene episulphoxide was prepared according to the reported method [12] and was recrystallized from hexane-chloroform (6:4) before use. Chlorotris(triphenylphosphine)-rhodium(I) and bromotris(triphenylphosphine)rhodium(I) were prepared as cited in the literature [13].

Preparation of Metal Complexes and their Reactions

(a) Preparation of $[\text{Rh}(\text{SO})\text{Cl}(\text{PPh}_3)]_2$

A solution of trans-stilbene episulphoxide (0.2 g, 1 mmole) in dichloromethane (15 ml) was slowly added to a stirred solution of chlorotris(triphenylphosphine)rhodium(I) (0.1 g, 0.1 mmole) in dichloromethane (20 ml) at 30°C under an argon atmosphere. The red-brown reaction mixture was refluxed for one and a half hours and the resulting solution was concentrated under reduced pressure to about 10 ml. On addition of petroleum ether (40-60°), a light brown complex got precipitated out which was centrifuged, washed several times with petroleum ether, n-hexane and dried in vacuum. It was recrystallized for constant melting point from dichloromethane-petroleum ether (1:3) with the yield of 30 mg (60%) after drying under vacuum (m.p. 210°C).

Anal. Calcd. for $[\text{Rh}(\text{SO})\text{Cl}(\text{PPh}_3)]_2$: C, 48.1; H, 3.3; S, 7.1; Cl, 8.0; P, 6.9; Rh, 22.9. Found: C, 47.8; H, 3.0; S, 6.8; Cl, 8.2; P, 6.8; Rh, 22.4%.

(b) Preparation of $[\text{Rh}(\text{SO})\text{Br}(\text{PPh}_3)]_2$

The procedure followed was the same as that for the chloro complex, except that $[\text{RhBr}(\text{PPh}_3)_3]$ was taken in the place of $[\text{RhCl}(\text{PPh}_3)_3]$. A brown complex (m.p. $196-198^\circ\text{C}$) was formed (yield, $\sim 55\%$) and from the washings, triphenylphosphine oxide triphenylphosphine sulphide and stilbene were recovered after evaporation.

Anal. Calcd. for $[\text{Rh}(\text{SO})\text{Br}(\text{PPh}_3)]_2$: C, 43.8; H, 3.0; S, 6.5; Br, 16.2; P, 6.3; Rh, 20.9. Found: C, 43.5; H, 2.8; S, 6.3; Br, 16.5; P, 5.9; Rh, 20.4%.

(c) Reaction of $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$ with excess of PPh_3

0.1 g (~ 0.1 mmole) of $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$ ($\text{X} = \text{Cl}$ or Br) was dissolved in 25 ml of benzene to which 0.3 g (~ 1 mmole) of triphenylphosphine was added. The clear solution was refluxed for 2 hours and the volume was reduced to about 10 ml under reduced pressure. On slow cooling to room temperature, a red-orange complex got settled down which was centrifuged, washed with ethyl alcohol, ether and dried under vacuum. It was identified to be $[\text{RhX}(\text{PPh}_3)_3]$ by analytical results and confirmed by comparing their infrared spectra, mixed melting point with authentic samples.

Anal. Calcd. for $[\text{RhCl}(\text{PPh}_3)_3]$: C, 70.1; H, 4.9; Cl, 3.9; P, 10.1. Found: C, 69.8; H, 4.5; Cl, 4.1, P, 9.8%.

Anal. Calcd. for $[\text{RhBr}(\text{PPh}_3)_3]$: C, 66.9; H, 4.6; Br, 8.3; P, 9.6. Found: C, 66.8; H, 4.4; Br, 8.6; P, 9.8% .

Analyses

Carbon, hydrogen, halogen and phosphorus estimations, melting points, infrared spectra and magnetic susceptibilities were obtained according to the methods quoted in Chapter III. All the analytical results are reported in their respective texts.

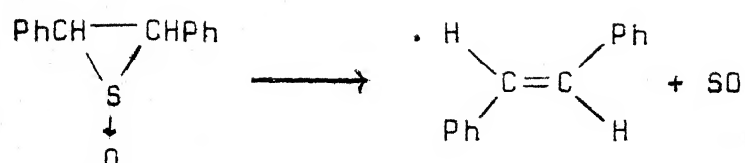
Conductivity Measurements

Conductivity measurements of the complexes were made on an Elico conductivity meter type CM-80 of millimolar solutions in nitrobenzene. All the compounds were found to be non-conducting to support their non-ionic nature.

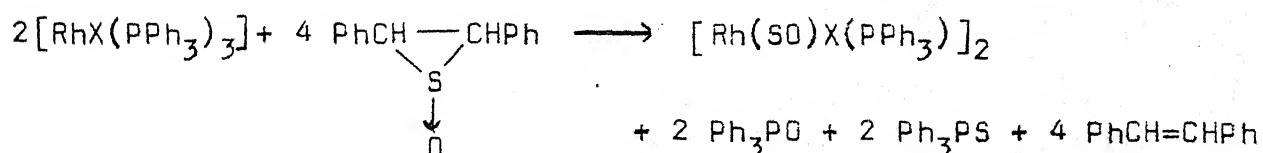
RESULTS AND DISCUSSION

The analytical data support the empirical formula of the type, $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]$ (where X = Cl or Br). In addition to these metallic complexes, triphenylphosphine oxide, triphenylphosphine sulphide and stilbene were recovered from the washings and identified as the major products of the reaction in each case. It is well documented to support the fact that trans-stilbene episulphoxide in dichloromethane and other solvents

undergoes decomposition to give stilbene and sulphur monoxide [8-11].



This sulphur monoxide can react with triphenylphosphine to form triphenylphosphine oxide and triphenylphosphine sulphide. It is, therefore, presumed that in the reaction medium, after the decomposition of episulphoxide, a part of sulphur monoxide is picked up by rhodium(I) complex and the rest of the SO combined with triphenylphosphine which may be present in the reaction medium, as a result of dissociation of the complex. The overall reaction may, therefore, be represented as follows:



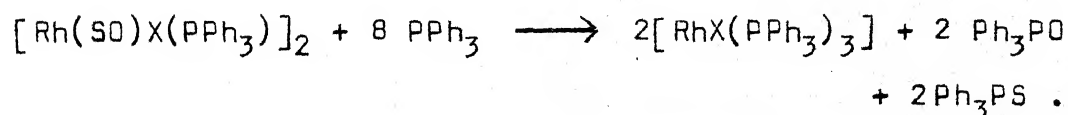
(where Ph = C₆H₅; X = Cl or Br).

Both complexes, (a) and (b) are air stable and their non-electrolytic nature in nitrobenzene solution shows the non-ionic nature of the compounds. The diamagnetism of both the complexes implies the fact that the rhodium atoms are either in +1 state or in +3 state. As the analytical data support the monohalo-compounds, rhodium is most likely to be present in +1 oxidation

state in these complexes. Both the complexes, (a) and (b) are found to be soluble in dichloromethane, chloroform, benzene and acetone and insoluble in ethanol, ether and n-hexane.

The infrared spectrum of the complex, (a) showed bands at 1040 cm^{-1} and 260 cm^{-1} along with the characteristic bands of triphenylphosphine. The bands at 1040 cm^{-1} and 260 cm^{-1} were assigned, respectively, to $\nu(\text{SO})$ [1,3] and $\nu(\text{Rh}-\text{Cl})$ (Cl trans to P or bridged chlorine or both). The absence of any band in the range between 300 cm^{-1} and 400 cm^{-1} ruled out the possibility of a terminal chlorine atom. The infrared spectrum of the complex, (b) showed a band at 1040 cm^{-1} , assignable to $\nu(\text{SO})$.

On treatment with excess of triphenylphosphine, the complexes, (a) and (b) decomposed to give $[\text{RhX}(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}$ or Br), $\text{Ph}_3\text{P}=\text{O}$ and $\text{Ph}_3\text{P}=\text{S}$ which further substantiated the presence of coordinated sulphur monoxide [1,3]:



LEGEND TO THE FIGURES

Fig. V.1 Infrared Spectra in KBr discs

(1) Stilbene episulphoxide

(2) $[\text{Rh}(\text{SO})\text{Cl}(\text{PPh}_3)]_2$

(3) $[\text{Rh}(\text{SO})\text{Br}(\text{PPh}_3)]_2$

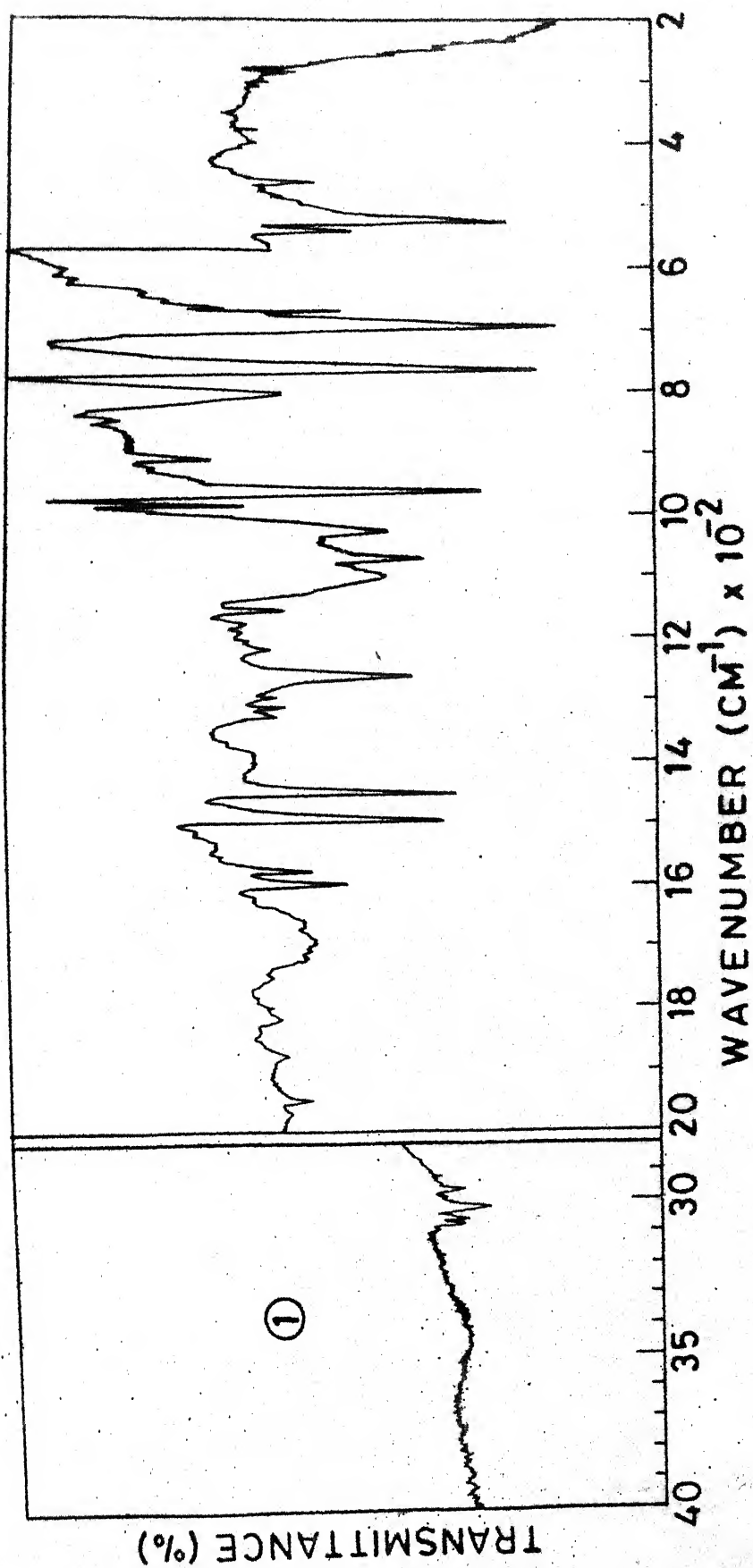


FIG. V.1 INFRARED SPECTRUM OF ①.

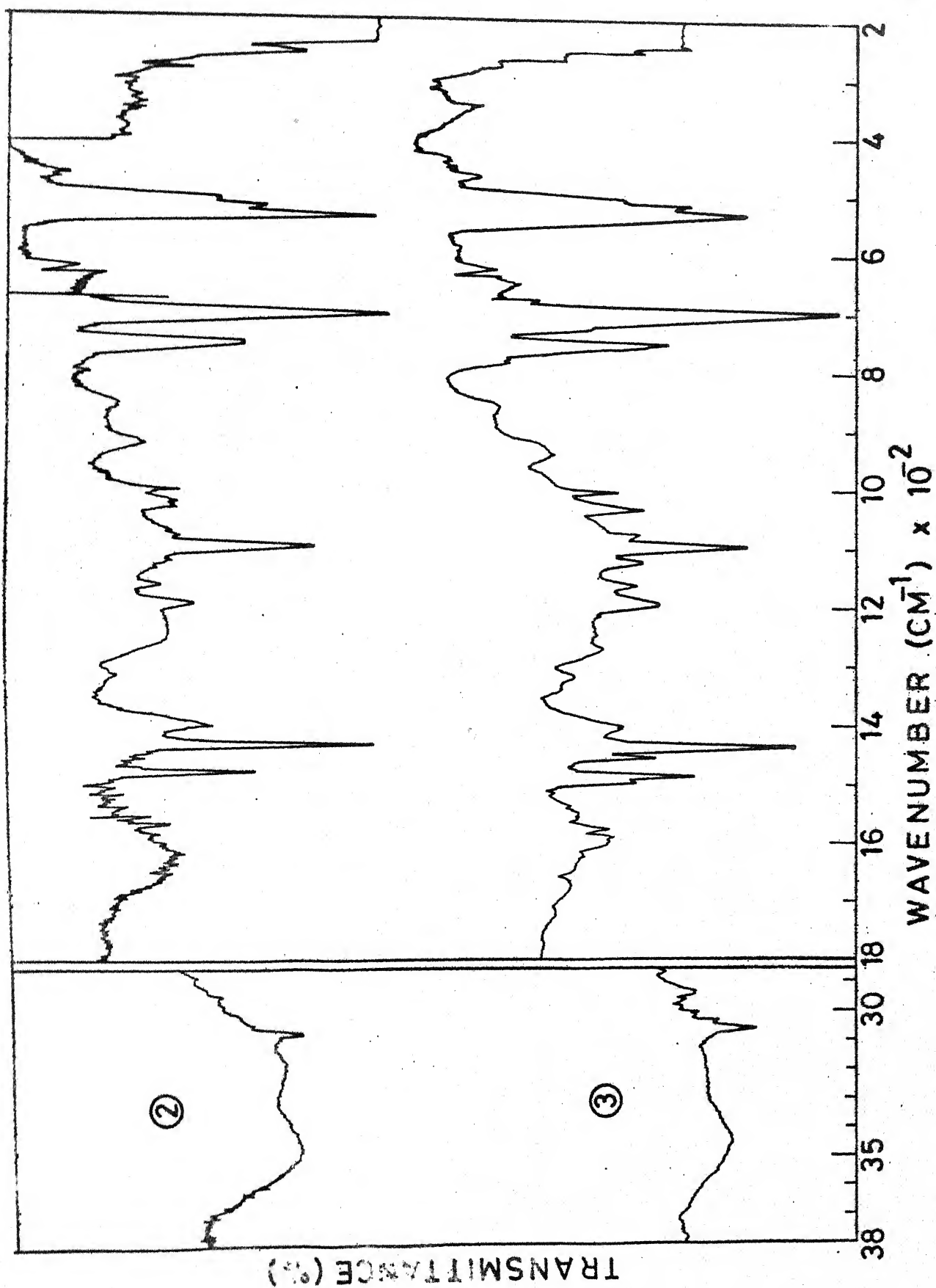


FIG. V.1 INFRARED SPECTRA OF ② & ③.

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CHAPTER VI

CHAPTER VI

SUMMARY and SCOPE FOR FURTHER WORK

The chemistry of sulphur containing ligands has been an area of active interest in the recent years. The understanding of the role of the metal ions which play in the long known biological and non-biological processes still remain a challenge before the mankind. In recent years an increasing interest has been to synthesize and to design new model ligands which could form metal complexes mimicing the properties found in biological and non-biological systems. During such a study it has been observed that the ligands containing sulphur or $-\overset{\text{H}}{\underset{|}{\text{N}}}-\text{CS}$ group not only play a significant role in them but have antiviral and antitumor activities as well. In addition, the biological

importance of metal-sulphur interaction is known in the sulphur containing amino acids bound to metal ions. Such compounds that involve in the catalysis of biological and non-biological processes claim the multifaceted chemistry of metal-sulphur bonds. These problems have led us to take up the study of different metal ion complexes with various types of sulphur-containing ligands which will assist in understanding the nature of such processes and the nature of metal-sulphur bond which still is in a confused state.

The present work is an attempt to seek a correlation between the various physico-chemical properties of the complexes with ligands having nitrogen or thiocarbonyl group as the potential coordination site. The main work centers on the synthetic, analytical and structural aspects of the metal complexes with sulphur containing ligands. The chosen ligands, for such an investigation, have the following sulphur containing moieties: (i) $-C(S)NHC(S)-$, (ii) $-NHC(S)SC_2H_5$, (iii) $-NSO$ and (iv) SO . The general binding characteristics and the different factors that influence the nature of the metal-sulphur bond have been briefly discussed. An overview of the metal complexes with sulphur containing ligands, analogous to Pyrrole-1,2-dithiodicarboximido and Ethyl N-phenyldithiocarbamate, has also been given in the Introduction.

The discussion of the ligand, pyrrole-1,2-dithiodicarboximide (PDD) along with its complexing behaviour with the complexes of $Fe(II)$, $Ru(II)$, $Ru(III)$, $Co(I)$, $Rh(I)$, $Ni(0)$, $Pd(0)$, $Pt(0)$,

Cu(I) and Ag(I) have been the subject matter of the second chapter. The complexes chosen for reactions with the ligand are such that they have either labile ligands or coordinatively vacant sites. In all the cases, they are found to give addition or substitution type of products with the ligand.

Dichlorobis(triphenylphosphine)iron(II), Dichlorotris(triphenylphosphine)ruthenium(II) and Trichlorobis(triphenylarsine)methanol-ruthenium(III) reacted with PDD to give complexes of the type, $[M(PDD)Cl_2(EPh_3)_2]$ (where $M = Fe, Ru$; $E = P, As$). Hydridotetrakis(triphenylphosphite)cobalt(I), Chlorotris(triphenylphosphine)rhodium(I) and Carbonylchlorobis(triphenylphosphine)rhodium(I), respectively gave $[Co(PDD)H(P(OPh)_3)_3]$, $[Rh(PDD)Cl(PPh_3)]$ and $[Rh(PDD)(CO)Cl(PPh_3)]$. Under dry nitrogen atmosphere $Ni(P(OPh)_3)_4$, $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ yielded the complexes of the type, $M(PDD)P_2$ (where $P = P(OPh)_3$ or PPh_3 , as the case may be). $CuCl(PPh_3)_3$ and $[Ag(PPh_3)_4](NO_3)$ gave respectively, $[Cu(PDD)Cl(PPh_3)]$ and $[Ag(PDD)(PPh_3)](NO_3)$.

Invoking the preferred geometries which the metal ions may take in their complexes, the analytical data suggested that the ligand is functioning as bidentate in some of the complexes and as monodentate in the remaining ones. To know the possible modes of linkages in these complexes, the infrared spectra of the ligand and complexes have been studied. From the study of the electronic spectra and magnetic moments data, the tentative geometries of the metal complexes have been proposed.

The details of the ligand, EPD and its complexing behaviour with various metal ions and certain metal ion complexes have been described in the third chapter. The possibility of the ligand to be monodentate in the resulting metal complexes has been supported by the analytical data. Metal salts of the type, MCl_2 ($M = Mn, Ni, Pt, Zn$ and Hg) reacted with EPD to give complexes, $M(EPD)_2Cl_2$. $FeCl_3$, $CoCl_2$, $RuCl_3$ and $RhCl_3$ yielded, respectively $Fe(EPD)_2Cl_2$, $Co(EPD)_2Cl_2 \cdot C_2H_5OH$, $Ru(EPD)_3Cl_2$ and $Rh(EPD)_3Cl_3$. A diamagnetic complex, $Rh(EPD)_2Cl(PPh_3)$ was formed as a result of the reaction of chlorotris(triphenylphosphine)rhodium(I) with the ligand. Tetrakis(triphenylphosphine)palladium(0) and tetrakis(triphenylphosphine)platinum(0) yielded the complexes of the type, $M(EPD)_2(PPh_3)_2$. $[Ag(EPD)_2](NO_3)$ and $Cd(EPD)_2I_2 \cdot EtOH$ were synthesized from $AgNO_3$ and CdI_2 . The mode of bonding of the ligand in the complexes and their geometries have been studied by infrared, electronic spectral and magnetic moments data.

The syntheses and the structural aspects of the complexes of N-sulphinylaniline (NSA) with certain metal salts and metal complexes have been embodied in the fourth chapter of the thesis. Although the N-sulphinyl group has been known in the form of organic sulphinylamines for quite sometime, covalent and ionic derivatives of other elements have been known only recently. Ketenes ($R_2C=C=O$), isocyanates ($R-N=C=O$) and isothiocyanates ($R-N=C=S$) are structurally related to N-sulphinylamines ($R-N=S=O$).

A pair of terminal cumulated unsaturated groups are present in these different classes of compounds and take part in a number of reactions in common. Addition reactions are restricted exclusively to the terminal unsaturated group.

N-Sulphinylaniline reacted with MnCl_2 and dichlorobis-(triphenylphosphine)iron(II) giving paramagnetic compounds, $\text{MnCl}_2(\text{NSA})_2$ and $\text{FeCl}_2(\text{PPh}_3)(\text{NSA})$, respectively. Ru(II) and Ru(III) complexes, $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuCl}_3(\text{AsPh}_3)_2 \cdot \text{CH}_3\text{OH}$ reacted with the ligand to give $\text{RuCl}_2(\text{PPh}_3)_2(\text{NSA})_2$ and $\text{RuCl}_2(\text{AsPh}_3)_2(\text{NSA})_2$, respectively. With cobalt(I) and rhodium(I) complexes, substitution products were obtained. Thus, it has been found that $\text{CoH}(\text{P}(\text{OPh})_3)_4$, $\text{RhCl}(\text{PPh}_3)_3$ and $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ gave, after the reaction with the ligand, $\text{CoH}(\text{P}(\text{OPh})_3)_2(\text{NSA})$, $\text{RhCl}(\text{PPh}_3)(\text{NSA})_2$ and $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)(\text{NSA})$, respectively. Complexes with metal ions in their formal zero oxidation states underwent substitution reactions with NSA. Tetrakis(triphenylphosphite)nickel(0), Tetrakis(triphenylphosphine)palladium(0) and Tetrakis(triphenylphosphine)platinum(0) afforded substitution products of the common type, $\text{M}(\text{P})_2(\text{NSA})_2$ (where $\text{P} = \text{PPh}_3$ or $\text{P}(\text{OPh})_3$). Copper(I) and silver(I) complexes, $\text{CuCl}(\text{PPh}_3)_3$ and $\text{Ag}(\text{PPh}_3)_4\text{NO}_3$ underwent substitution reactions with NSA giving $\text{CuCl}(\text{PPh}_3)_2(\text{NSA})$ and $[\text{Ag}(\text{PPh}_3)(\text{NSA})](\text{NO}_3)$, respectively.

N-Sulphinylaniline has been found to bond with various metal ions, mostly through the nitrogen atom of the N-sulphinyl

group. Comparison was made between the infrared data of the ligand and those of the complexes. Considerable shifts of N=S=O bands in the spectra of the complexes led to invoke the involvement of nitrogen in the bonding with the metal ions in these complexes.

Preparation and characterization of rhodium(I) complexes with sulphur monoxide as ligand have been the content of fifth chapter. The stabilization of dimeric sulphur monoxide rhodium(I) complexes have been described as a consequence of the reaction between trans-stilbene episulphoxide and $[\text{RhX}(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}, \text{Br}$). The reported phenomenon of producing sulphur monoxide from stilbene episulphoxide has been used as the source of SO for the purpose of trapping and isolating the sulphur monoxide complex.

As a result of the reaction between trans-stilbene episulphoxide and $[\text{RhX}(\text{PPh}_3)_3]$ ($\text{X} = \text{Cl}, \text{Br}$) in dichloromethane, the isolated complexes are of the type, $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$. In these reactions, the other major products were found to be triphenylphosphine oxide, triphenylphosphine sulphide and trans-stilbene. It is reasoned to presume that a portion of sulphur monoxide present in the medium was picked up by the coordinatively unsaturated rhodium(I) complex to form the complex containing SO as ligand. Infrared bands present in both product complexes (chloro- and bromo-) around 1040 cm^{-1} were taken to support the presence of coordinated SO. The

products are reported to be dimers based on other physico-chemical studies.

All the products formed during the reactions were characterized by elemental analyses, infrared spectra, magnetic moments and conductivity measurements. The reported complexes along with their colours, possible geometries and bonding scheme have been summarized in the Table I.1.

For further studies, we would propose to extend the work to various other systems as follows:

(a) Triphenylarsine and triphenylstibine analogues of the above reported complexes can also be prepared and their physicochemical properties could be compared.

(b) Further synthetic endeavours like adduct formation with ligands having different electronic and steric characteristics could also provide another breed of complexes.

(c) Stability constant studies of these complexes may also prove worthwhile for their possible application in analytical as well as in industrial fields.

(d) As most of the insecticides are potential chelating agents, a major portion of insecticides sprayed over the crops form stable, water insoluble metal chelates of earth's mineral, thereby depriving the crops of their essential micro-nutrients. Study of metal chelates as those that are embodied in this thesis, has a promise in the fields of crop research also.

(e) A vast number of Pt(II) complexes have been screened for antitumor activity; virtually all have been of four coordinate square planar geometry. Such compounds are direct analogues of the proto type antitumor platinum complex, cis-dichlorodiammine platinum(II), available clinically as 'cis-platin' or 'platinol'. Without any dint of doubt, the road to finding solution to cancer problems has been very rough and unpredictable. Since it is a battle whose end is not immediately at hand, synthesis and characterization of new varieties of square planar platinum(II) complexes could be a humble contribution towards meeting the challenge of the present medical need.

LIST OF PUBLICATIONS

1. Stable Dimeric Complexes with Sulphur Monoxide Ligand: Formation of $[\text{Rh}(\text{SO})\text{X}(\text{PPh}_3)]_2$ ($\text{X} = \text{Cl}$ or Br),
Kilakathi S. Arulsamy, Krishna K. Pandey, and
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2. Complexes of Pyrrole-1,2-dithiodicarboximide with $\text{Fe}(\text{II})$,
 $\text{Co}(\text{I})$, $\text{Ni}(\text{O})$, $\text{Cu}(\text{I})$, $\text{Ag}(\text{I})$, $\text{Ru}(\text{II})$, $\text{Rh}(\text{I})$, $\text{Pd}(\text{O})$ and
 $\text{Pt}(\text{O})$,
K.S. Arulsamy, R.F.N. Ashok and U.C. Agarwala
(under preparation).
3. Ethyl N-Phenyldithiocarbamate Complexes of $\text{Fe}(\text{III})$, $\text{Ru}(\text{II})$,
 $\text{Co}(\text{II})$, $\text{Rh}(\text{I})$, $\text{Rh}(\text{III})$, $\text{Ni}(\text{II})$, $\text{Pd}(\text{O})$, $\text{Pt}(\text{O})$, $\text{Pt}(\text{II})$ and
 $\text{Ag}(\text{I})$,
K.S. Arulsamy, R.F.N. Ashok and U.C. Agarwala
(under preparation).
4. Complexing Behaviour of N-Sulphinylaniline: Complexes
of $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Ru}(\text{II})$, $\text{Co}(\text{I})$, $\text{Rh}(\text{I})$, $\text{Ni}(\text{O})$, $\text{Pd}(\text{O})$,
 $\text{Pt}(\text{O})$, $\text{Cu}(\text{I})$ and $\text{Ag}(\text{I})$,
K.S. Arulsamy, R.F.N. Ashok and U.C. Agarwala
(under preparation).